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April 21, 2006

Mr. John S. Nohrstedt
U.S. Army Corps of Engineers
Engineering and Support Center, Huntsville
4820 University Square
Huntsville, AL 35816-1822

SUBJECT: Revised Final Generic Site-Wide Sampling and Analysis Plan for the Seneca Army Depot Activity; Contract DACA87-02-D-0005, Delivery Order 0013

Dear Mr. Nohrstedt:

Parsons is pleased to submit responses to comments from NYSDEC on the Final Generic Site-Wide Sampling and Analysis Plan for the Seneca Army Depot Activity located in Romulus, New York. Please find enclosed replacement pages to update the report. Instructions are provided. In addition to the enclosed replacement pages, the Revised Final Generic Site-Wide Sampling and Analysis Plan for the Seneca Army Depot Activity is being submitted electronically.

This Generic Site-Wide Sampling and Analysis Plan was prepared in accordance with the Scope of Work for Delivery Order 0013 under Contract DACA87-02-D-0005. Once approved, it is Parsons' intention to use this generic site-wide document for activities performed for the Seneca Army Depot Activity. This Generic Site-Wide Sampling and Analysis Plan will be used together with site-specific work plans for various projects for the Seneca Army Depot Activity.

Parsons appreciates the opportunity to provide you with the Revised Final Generic Site-Wide Sampling and Analysis Plans for this work. Should you have any questions, please do not hesitate to call me at (617) 449-1405 to discuss them.

Sincerely,

Todd Heino, P.E.
Project Manager

Enclosure

cc: S. Absolom, SEDA
C. Boes, USAEC
J. Fallo, USACE, NY District
K. Hoddinott, USACHPPM
R. Battaglia, USACE, NY District
T. Enroth, USACE, NY District

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April 21, 2006

Mr. Julio Vazquez
USEPA Region II
Superfund Federal Facilities Section
290 Broadway, 18th Floor
New York, NY 10007-1866

Mr. Kuldeep K. Gupta, P.E.
New York State Department of Environmental Conservation (NYSDEC)
Division of Environmental Remediation
Remedial Bureau A, Section C
625 Broadway
Albany, NY 12233-7015

Ms. Charlotte Bethoney
Bureau of Environmental Exposure Investigation
Flanigan Square, Room 300
547 River Street
Troy, NY 12180

SUBJECT: Revised Final Generic Site-Wide Sampling and Analysis Plan for the Seneca Army Depot Activity; Contract DACA87-02-D-0005, Delivery Order 0013

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Todd Heino, P.E.
Program Manager

Enclosure
cc: S. Absolom, SEDA
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J. Nohrstedt, USACE, Huntsville
K. Hoddinott, USACHPPM
R. Battaglia, USACE, NY District
T. Enroth, USACE, NY District
J. Fellinger, Contractor for USEPA

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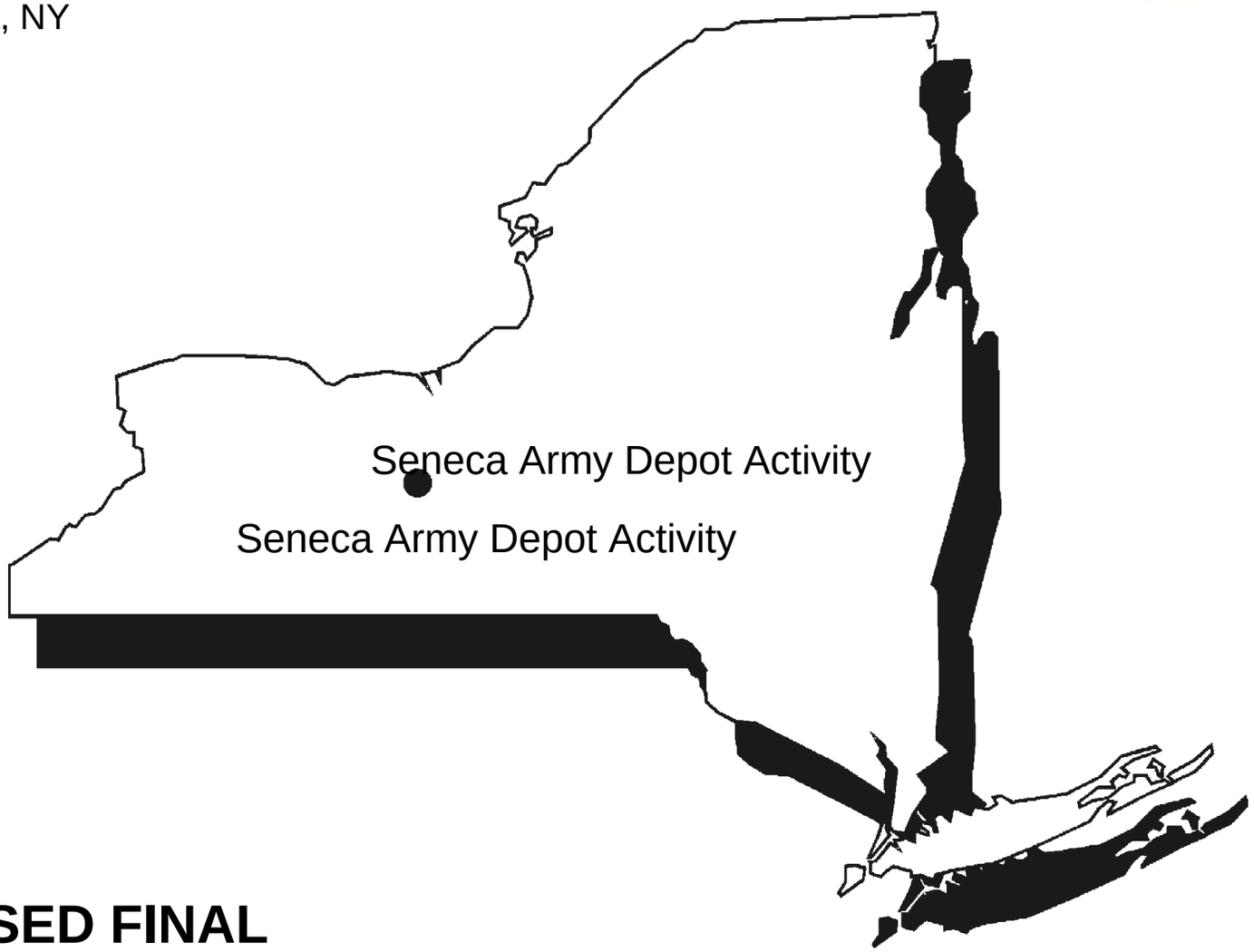
US Army, Engineering & Support Center
Huntsville, AL

00165

Seneca Army Depot Activity
Romulus, NY



REVISED FINAL

GENERIC SITE-WIDE SAMPLING AND ANALYSIS PLAN VOLUME I & II

SENECA ARMY DEPOT ACTIVITY

EPA Site ID# NY0213820830
NY Site ID# 8-50-006
CONTRACT NO. DACA87-02-D-0005
DELIVERY ORDER NO. 0013

PARSONS
APRIL 2006

REVISED FINAL
GENERIC SITE-WIDE SAMPLING AND ANALYSIS PLAN
SENECA ARMY DEPOT ACTIVITY
ROMULUS, NEW YORK

April 21, 2006

Prepared by:

PARSONS
150 Federal Street
Boston, MA 02110
617-946-9400

EPA SITE ID# NY0213820830
NY SITE ID# 8-50-006
CONTRACT NUMBER DACA87-02-D-0005
DELIVERY ORDER NO. 0013

Reviewed and Approved by:

_____ 04/19/06

Todd Heino, Parsons Project Manager, Date

_____ 04/19/06

John Lanier, Parsons Quality Assurance Officer Date

_____ 04/19/06

Chunhua Liu, Parsons Project Chemist Date

_____ _____

Julio F. Vazquez, USEPA Region 2 Project Manager Date

_____ _____

Kuldeep K. Gupta, NYSDEC Project Manager Date

_____ _____

John S. Nohrstedt, USACE, Huntsville Date

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ACRONYMS

A2LA	American Association of Laboratory Accreditation
A-E	Architect-Engineer
AA	Atomic Absorption
ARAR	Applicable or Relevant and Appropriate Requirement
ASP	Analytical Service Protocol
ASTM	American Society for Testing and Materials
ATV	all-terrain vehicle
BIP	blow in place
BRAC	Base Realignment and Closure
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulation
CCV	Continuing Calibration Verification
CLP	Contract Laboratory Program
COC	Chain-Of-Custody
COR	Contracting Officer's Representative
cpm	counts per minute
CRQL	Contract Required Quantitation Limit
CY	Calendar Year
DER	Division of Environmental Remediation
DID	Data Item Description
DLA	Defense Logistics Agency
DO	Dissolved Oxygen
DOA	Department of the Army
DoD	Department of Defense
DOT	Department of Transportation
dpm/100 cm^2	decays per minute per 100 square centimeters
DQI	Data Quality Indicator
DQO	Data Quality Objectives
DQOP	Data Quality Objectives Process
EDD	Electronic Data Deliverable
ELAP	Environmental Laboratory Approval Program
EM	Electromagnetic
EOD	Explosive Ordnance Disposal
ESS	Explosive Safety Submission
eV	electrical volts
FB	Field Blank

FFA	Federal Facilities Agreement
FID	Flame Ionization Detector
FSP	Field Sampling Plan
ft.	feet or foot
gal	gallon(s)
GALP	Good Automated Laboratory Practices
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GPR	Ground Penetrating Radar
GPS	Global Positioning System
GM	Geiger-Mueller
HAZWOPER	Hazardous Waste Operator and Emergency Response
HP/RSO	Health Physicist/Radiological Safety Officer
HSA	Hollow Stem Augers
HTRW	Hazardous, Toxic and Radioactive Waste
HPLC	High Performance Liquid Chromatography
lbs/gal	pounds per gallon
IC	Ion Chromatography
ICAL	Initial Calibration
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectra
ICP-MS	Inductively Coupled Plasma-Mass Spectra
ICS	Interference Check Sample
I.D.	inside diameter
ID	Identification
IDW	Investigation Derived Waste
IS	Internal Standard
LCS	Laboratory Control Sample
MB	Matrix Blank
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
MGFD	Maximum Generated Fragmentation Distance
MI	Manual integration
mL	Milliliter
mL/L	milliliters per liter
ml/min	milliliters per minute (ml/min)
MPPEH	material posing potential explosive hazard
MS	Mass Spectrometry/Matrix Spike
MSD or MD	Matrix Spike Duplicate

MS/MSD	Matrix Spike/Matrix Spike Duplicate
MW	monitoring well or monitoring well boring
mV	milli volt
NAD	North American Datum
NAPL	Non-Aqueous Phase Liquid
NAVD	North American Vertical Datum
NCP	National Contingency Plan
NGVD	National Geodetic Vertical Datum
NIST	National Institute Standards and Technology
NIOSH	National Institute for Occupational Safety and Health
NPL	National Priorities List
NTU	Nephelometric Turbidity unit
NY	New York
NYCRR	New York State Codes, Rules and Regulations
NYSDEC	New York State Department of Environmental Conservation
NYSDOH	New York State Department of Health
OE	Ordnance and Explosives
ORP	Oxidation-Reduction Potential
OSHA	Occupational Safety and Health Administration
OVM	Organic Vapor Monitor
PAB	Project Analytical Batch
PAH	Polynuclear Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
pCi/g	picocuries per gram
PDOP	Position Dilution of Precision
PE	Performance Evaluation
PHC	Petroleum Hydrocarbons
PID	Photoionization Detector
PM_{10}	Particulate matter less than 10 µm aerodynamic diameter
ppb	parts-per-billion
PPE	Personal Protective Equipment
ppm	parts-per-million
PQL	Practical Quantitation Limit
PQO	Project Quality Objectives
PRG	Preliminary Remediation Goal
PUF	Polyurethane Foam
PVC	Polyvinyl Chloride
QA	Quality Assurance
QAO	Quality Assurance Officer

QAPP	Quality Assurance Program Plan
QA/QC	Quality Assurance/ Quality Control
QC	Quality Control
QL	Quantitation Limit
RBC	Risk Base Concentrations
RCRA	Resource Conservation and Recovery Act
RF	Response Factor
RIC	Reconstructed Ion Chromatograms
RI/FS	Remedial Investigation/Feasibility Study
RL	Reporting Limit
RQD	Rock Quality Designation
RPD	Relative Percent Difference
RT	Retention Time
RTK	Real Time Kinematic
RTS	Robotic Total Station
SAP	Sampling and Analysis Plan
SB	Soil Boring
SCG	Standards, Criteria, and Guidance
SD	Sediment
SDG	Sample Delivery Group
SEDA	Seneca Army Depot Activity
SOP	Standard Operating Procedures
SOW	Statement of Work
SPP	Systematic Planning Process
SQL	Sample Quantitation Limit
SS	Surface Soil
SS-WP	Site Specific Work Plan
STARS	Spill Technology and Remediation Series
SUXOS	Senior UXO Supervisor
SVOC	Semivolatile Organic Compound
SW	Surface Water
SWMU	Solid Waste Management Unit
TAGM	Technical and Administrative Guidance Memorandum
TB	Trip Blank
TBC	To Be Considered
TCL	Target Compound List
TCLP	Toxicity Characteristic Leaching Procedure
TIC	Tentatively identified compound
TKN	Total Kjeldahl Nitrogen

TOC	Total Organic Carbon
TOGS	Technical Operating Guidance Series
TSP	Total Suspended Particulate
TP	Test Pit
TPH	Total Petroleum Hydrocarbon
UFPO	Under Ground Facilities Protection Organization
ug/Kg	micrograms per kilogram
ug/L	micrograms per liter
µm	micrometer
U.S.	United States of America
USACE	United States Army Corps of Engineers
USAESCH	US Army Engineering and Support Center, Huntsville
USCS	Unified Soil Classification System
USDoD	United States of America Department of Defense
USDoE	United States of America Department of Energy
USDoI	United States Department of the Interior
USEPA	United States Environmental Protection Agency
USNRC	United States Nuclear Regulatory Commission
UXO	Unexploded Ordnance
UXOQCS	UXO Quality Control Specialist
UXOSO	UXO Safety Officer
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
VTSR	verified time of sample receipt
WB	Wash or Rinse Blank
WP	Work Plan

1.0 INTRODUCTION

Parsons has prepared the Generic Site-Wide Sampling and Analysis Plan (SAP) for the Seneca Army Depot Activity (SEDA) in Romulus, New York. This generic site-wide SAP will serve as an umbrella document under which project-specific tasks are conducted. Project-specific information is not covered in this generic site-wide SAP but is documented in detailed project-specific work plans, which use the generic SAP as an informational reference whenever appropriate. The use of this generic SAP, with supplemental project-specific work plans as needed, is a significant opportunity to use a graded approach, reducing repetition and streamlining the SAP development, review, and approval process.

The SAP mainly consists of two parts: Quality Assurance Program Plan (QAPP, Sections 2 through 15) and Field Sampling Plan (FSP, Section 16).

The generic QAPP prepared for the Seneca Army Depot Activity states the expectations and specifications for obtaining the type and quality of environmental data needed for the project and describes the policies and procedures for ensuring that work process, products, or services satisfy the stated expectations and specifications. The QAPP includes definitions and generic goals for data quality and minimum requirements for quality assurance/ quality control (QA/QC) samples. The FSP provides general information and standard operating procedures (SOPs) applicable to sampling and analytical activities to be performed at all sites at SEDA.

It should be noted that the SAP may include discussions on procedures or methods that are not applicable to a specific site since it is intended to encompass all sites at the Seneca Army Depot. A Site-Specific work plan (SS-WP) will be prepared for each individual site where sampling and analytical activities are being conducted. The work plan will serve as addenda to this SAP. It is intended that once the SAP is finalized, it will not be modified (except for programmatic changes) and will serve as a programmatic document. Site-specific sampling information and any exceptions or proposed changes to the SAP will be addressed and included in the site-specific work plan. The majority of information contained in this SAP should not be repeated in the SS-WP. The methods specific to each site should specify the appropriate detection limit and reporting limit information. Any deviations from this SAP (e.g., holding times, detection limits, sampling methods, etc.) should be brought to the attention of the management team.

The SS-WP should not be a stand-alone document from this SAP. This SAP will provide the majority of the QA/QC information; the SS-WP should simply supplement this information by providing site-specific requirements. Section 17 of this SAP summarizes key elements that should be included in the SS-WP.

The Seneca Site-Wide SAP is prepared consistent with the guidance including, but not limited to, the following:

- Guidance for the Data Quality Objectives Process, United States Environmental Protection Agency (USEPA) QA/G-4, 2000a
- USEPA Requirements for Quality Assurance Project Plans, USEPA QA/R-5, 2001a
- Data Quality Objectives Process for Hazardous Waste Site Investigations, USEPA QA/G-4HW, 2000c
- Uniform Federal Policy for Quality Assurance Project Plans, Evaluating, Assessing, and Documenting Environmental Data Collection and Use Programs, USEPA, 2005a
- Guidance for Quality Assurance Project Plans, USEPA QA/G-5, 2002b
- Quality Management Plan for Western Ecology Division, USEPA, 2001b
- Guidance for the Development of Quality Assurance Project Plans for Environmental Monitoring Projects, USEPA Region 2, 2004
- Analytical Service Protocols (ASP), New York State Department of Environmental Conservation (NYSDEC), 2000
- Technical Guidance for Site Investigation and Remediation SW-96-09: Development and Review of Site Analytical Plans, NYSDEC, 2001
- Draft DER-10 Technical Guidance for Site Investigation and Remediation, NYSDEC, 2002
- Chemical Quality Assurance for Hazardous, Toxic and Radioactive Waste (HTRW) Project, United States Army Corps of Engineers (USACOE) EM200-1-6, 1997
- Requirements for the Preparation of Sampling and Analysis Plan, USACOE EM200-1-3, 2001

Appendix A presents a cross reference table for selected applicable SAP guidance.

2.0 PROJECT DESCRIPTION

2.1 SENECA ARMY DEPOT PROJECT BACKGROUND

SEDA is located approximately 40 miles south of Lake Ontario, near Romulus, New York (Figure 1). The Depot lies immediately west of the village of Romulus, New York (NY), 12 miles south of the villages of Waterloo and Seneca Falls, and 2.5 miles north of the village of Ovid, NY. The two closest major cities are Rochester, NY, which is located approximately 60 miles northwest, and Syracuse, NY, which is located approximately 60 miles northeast, respectively.

SEDA is located in an uplands area, where the elevation ranges from approximately 600 feet (ft.) National Geodetic Vertical Datum (NGVD 1929) along the western boundary of the Depot to nearly 760 feet NGVD 1929 in the central portion of the eastern boundary. The uplands area where SEDA is located forms a divide separating two of the New York Finger Lakes; Cayuga Lake on the east and Seneca Lake on the west. Sparsely populated farmland covers most of the surrounding area. New York State Highways 96 and 96A border SEDA to the east and west, respectively. Figure 2 presents a plan view of SEDA.

The 10,587-acre SEDA facility has been owned by the United States Government since 1941 and was operated by the Department of the Army (DOA) until 2001. From its inception in 1941 until 1995, SEDA's primary mission was the receipt, storage, maintenance, and supply of military items, including munitions and equipment. Seneca Army Depot was proposed to be included on the National Priorities List (NPL) on July 14, 1989. Once Seneca Army Depot was listed on the NPL, the Army, USEPA, and NYSDEC identified a list enumerating 57 solid waste management units (SWMUs) where historic data or information suggested, or evidence existed to support, that hazardous materials or hazardous wastes had been handled and may have possibly been released and migrated into the environment. Each of these sites was identified in the Federal Facilities Agreement (FFA) (Army, USEPA, NYSDEC, 1993) signed by the three parties, and this list subsequently expanded to include 72 sites. Activities at the SEDA are regulated by the Comprehensive Environmental Response, Compensation, and Liability Act of (CERCLA) and Resource Conservation and Recovery Act (RCRA). USEPA and NYSDEC are the approval entities for the project. The site number is listed as NY0213820830 and 8-50-006 under the USEPA and NYSDEC program, respectively.

The Depot’s mission changed in early 1995 when the Department of Defense (DoD) recommended closure of the SEDA under the Base Realignment and Closure (BRAC) process. This recommendation was approved by Congress on September 28, 1995, and the Depot was closed by July 2001.

This project is conducted by Parsons under the Huntsville Contract titled Architect-Engineer (A-E) Services for Investigative and Design Expertise for Indefinite Delivery/Indefinite Quality Contract for Environmental Programs at Defense Logistics Agency (DLA) Field Activities and Other DoD Activities (DACA87-02-D-0005).

A field sampling and analysis plan and a chemical data acquisition plan, developed in 1995 as a generic FSP and a generic QAPP for the Seneca Army Depot Activity, was incorporated in the Final Generic Installation Remedial Investigation/Feasibility Study (RI/FS) Workplan (Parsons, 1995) as Appendix A and Appendix C, respectively. This SAP, once approved, will supercede the current field sampling and analysis plan and the chemical data acquisition plan developed in 1995.

2.2 PROJECT SPECIFIC BACKGROUND

Background information for each specific site within the Depot will be included in the SS-WP. The SS-WP will present information of site location, site contamination history, and findings from previous investigations.

2.3 PROJECT SCOPE AND OBJECTIVES

The primary objective of the project is to conduct remedial investigation, feasibility study, and remedial action at the identified SWMUs at Seneca Army Depot. Work required includes activities such as but not limited to investigation, testing, excavation, separation, treatment, and disposal of contaminated materials. Work will be conducted in accordance with the FFA (USEPA, NYSDEC, Army, 1993), CERCLA, RCRA, National Oil and the Hazardous Substances Contingency Plan (more commonly called the National Contingency Plan, or NCP) requirements, with regulatory coordination of the NYSDEC and the USEPA Region 2.

2.4 APPLICABLE REGULATIONS/STANDARDS

Applicable or Relevant and Appropriate Requirements (ARARs) are promulgated regulatory standards or requirements and as such are legally enforceable and generally applicable and equivalent to the media or conditions at the site. In addition to ARARs, advisories, criteria, or guidance may be evaluated as "To Be Considered" (TBC) regulatory items. CERCLA indicates that the TBC category could include advisories, criteria, or guidance that were developed by USEPA, other federal agencies, or states that may be useful in developing CERCLA remedies. The following ARARs and TBCs have been identified for the project.

Soils/Sediment

- NYSDEC Technical and Administrative Guidance Memorandum (TAGM) HWR-94-4046 (January 1994) – TBC,

- EPA Regional Preliminary Remediation Goals (PRGs) or Risk Based Concentrations (RBCs) – TBC.
- NYSDEC Technical Guidance for Screening Contaminated Sediments. Updated 1999.

Groundwater/Surface Water

- Technical Operating Guidance Series (TOGS), 1.1.1, Class GA (groundwater) or Class C (surface water) Standards (June 1998 with amendments) – ARAR
- National Primary Drinking Water Regulations - ARAR
- Technical Operating Guidance Series (TOGS), 1.1.1, Class GA (groundwater) or Class C (surface water) Guidance Values (June 1998 with amendments). - TBC
- National Recommended Water Quality Criteria – TBC

Potentially applicable ARARs and TBCs are provided in Table 1-A and 1-B for soils/sediment and groundwater/surface water, respectively.

3.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

3.1 PROJECT ORGANIZATION

The organizations who will be directly involved in the performance of the SEDA projects will include the NYSDEC, USEPA Region 2, the Army, SEDA, Parsons, and subcontractors. The organizations, key personnel from each organization, and personnel contacts are listed in the following table. A chart showing the project organization is presented in Figure 3. Project-specific responsibilities (to include any additional subcontractors) and project-specific team will be identified and discussed in detail in the SS-WP.

Organization	Position	Name & Address	Responsibility	Phone	Fax	Email
USACE Huntsville	Project Manager	John Nohrstedt	Project Management			John.Nohrstedt@hnd01.usace.army.mil
Seneca Army Depot Activity	BRAC Environmental Coordinator	Stephen Absolom Seneca Army Depot Activity, 5786 State Rte 96, P.O. Box 9 Romulus, New York 14541-0009	Project Coordination	607-869-1309	607-869-1362	stephen.m.absolom@us.army.mil
USACE, NY District	Project Manager	Thomas Battaglia Seneca Army Depot Activity, 5786 State Rte 96, Building 125 Romulus, New York 14541-0009	Project Coordination, fund programming	607-869-1353	607-869-1251	thomas.c.battaglia@nan02.usace.army.mil
USACE, NY District	Project Manager	Janet Fallo Seneca Army Depot Activity, 5786 State Rte 96, Building 125 Romulus, New York 14541-0009	Project Coordination, fund programming	607-869-1248	607-869-1251	Janet.R.Fallo@nan02.usace.army.mil
USACE, NY District	Project Manager	Randall Battaglia Seneca Army Depot Activity, 5786 State Rte 96, Building 125 Romulus, New York 14541-0009	Project Coordination, fund programming	607-869-1523	607-869-1251	randy.w.battaglia@nan02.usace.army.mil

Organization	Position	Name & Address	Responsibility	Phone	Fax	Email
USACE, NY District	Project Manager	Thomas Enroth Seneca Army Depot Activity, 5786 State Rte 96, Building 125 Romulus, New York 14541-0009	Project Coordination, fund programming	607-869-1255	607-869-1251	Thomas.R.Enroth@nan02.usace.army.mil
Parsons	Project Manager	Todd Heino 150 Federal Street, Boston, MA 02110	Overall project coordination	617-449-1405	617-946-9777	todd.heino@parsons.com
Parsons	Technical Director	Douglas Downey 1700 Broadway, Suite 900 Denver, CO	Provide technical recommendation	(303) 764-1915	(303) 831 8208	Doug.Downey@parsons.com
Parsons	Quality Assurance Officer	John Lanier 180 Lawrence Bell Dr, Suite 104 Williamsville, NY 14221	Overall QA implementation	716-633-7074 X 222	716-633-7195	John.Lanier@parsons.com
Parsons	Field Team Leader	Tom Andrews 180 Lawrence Bell Dr., Suite 104 Williamsville, NY 14221	Construction oversight	716-633-7074	716-633-6195	Tom.Andrews@parsons.com
Parsons	Database researcher	Eric Bishop 2701 Liberty Parkway, Suite 317 Midwest City, OK 73110-2880 Brendan Baranek-Olmstead 150 Federal Street Boston, MA 02110	Database management	405-732-9803 617-449-1404	405-732-9726 617-946-9777	Eric.Bishop@parsons.com Brendan.Baranek-Olmstead@parsons.com
Parsons	Project Chemist	Chunhua Liu 150 Federal Street Boston, MA02110	Data Evaluation, Laboratory Coordination	617-449-1567	617-946-9777	Chunhua.liu@parsons.com
Parsons	Field Analyst	Ben McAllister 150 Federal Street, Boston, MA 02110	Field Analysis	617-946-1592	617-946 - 9777	benedict.mcallister@parsons.com
Laboratory	Laboratory Manager	TBD	Laboratory Analyses	TBD	TBD	TBD

Organization	Position	Name & Address	Responsibility	Phone	Fax	Email
NYSDEC	Project Manager	Kuldeep K. Gupta 625 Broadway Albany, NY 12233-7015	Supervision, review, and approval	518-402-9620		kxgupta@gw.dec.state.ny.us
USEPA Region 2	Project Manager	Julio F. Vazquez 290 Broadway, 18th Floor New York, NY 10007-1866	Supervision, review, and approval	212-637-4323	212-637-3256	vazquez.julio@epamail.epa.gov

3.2 ROLES AND RESPONSIBILITIES

3.2.1 USEPA and NYSDEC

For the Seneca Depot Activity, NYSDEC and USEPA are the primary regulatory agencies with responsibilities for administering the site activities. These agencies will receive copies of the SAP. All applicable communication and reports will be delivered from Parsons to SEDA for delivery to NYSDEC and USEPA. NYSDEC and USEPA are responsible for the final acceptance of all documents with authority under CERCLA and RCRA.

3.2.2 USACE, Huntsville

Huntsville is responsible for the Seneca project oversight. The overall Point of Contact for Seneca Depot activities, or the Contracting Officer's Representative (COR), is Mr. John Nohrstedt. Mr. John Nohrstedt or his designee will provide day-to-day liaison with the Huntsville and ensure that appropriate coordination is maintained among the different parties involved in the project.

3.2.3 SEDA

SEDA is responsible for coordinating the activities at the Depot and has the responsibility of reviewing all supporting documents. Mr. Stephen Absolom has been designated as the installation manager for SEDA and he is responsible for ensuring that the Army's objectives are being met. Mr. Absolom or his designee is responsible for programming funds, establish and maintain information repository, public involvement, and regulator and stakeholder coordination.

3.2.4 USACE, NY District

USACE, NY District provides funding and technical support to SEDA. Mr. Randall Battaglia, Ms. Janet Fallo, Mr. Thomas Enroth, and Mr. Thomas Battaglia are project managers that oversee various

projects at Seneca in support of Mr. Absolom at SEDA. Mr Randall Battaglia coordinates with USACE Huntsville in providing the necessary funding for projects at SEDA.

3.2.5 Parsons

Parsons has been contracted for the Seneca Army Depot remediation activity and will be responsible for preparing documents and overall implementation of the remediation/investigation. Parsons team consists of members who have extensive experience in conducting site investigation/remediation. Key personnel and their respective roles and responsibilities are discussed below.

3.2.5.1 Project Manager

Mr. Todd Heino will serve as the Parsons project manager and will have overall responsibility for implementing the project. The Boston office of Parsons is responsible for conducting the work under the contract and will be supported by other Parsons offices as needed. Mr. Todd Heino is responsible for directing, overseeing, and coordinating all project activities. He will coordinate all efforts on this project including contact with the SEDA project manager, travel for the project team, and submission of all deliverables. Mr. Todd Heino is responsible for submitting QAPPs and QAPP revisions and amendments to appropriate personnel for review and approval.

3.2.5.2 Project Team

Parsons project team consists of technical personnel, including field sampling personnel, quality assurance officer, project chemist, geologists, chemists, risk assessors, and engineer designers. The project team is responsible for providing all the information required by the SAP and for resolving all technical issues for the project. All project personnel are responsible for implementing the SAP, and for reporting all deviation from the SAP to the project manager. Corrective action procedures must be implemented when deviations from the SAP are noted or whenever project personnel identify field sampling or analytical problems that could potentially affect data quality or usability.

Technical Director

Mr. Doug Downey will perform duties of Technical Director for the SEDA activities. As Technical Director, Mr. Downey or his designee will provide technical guidance and oversight for all field activities, and will conduct field audits and coordinate any corrective actions with the project manager.

Quality Assurance Officer

In accordance with the NYSDEC Technical Guidance for Site Investigation and Remediation (2002), a quality assurance officer (QAO) with the qualifications specified in the NYSDEC guidance has been assigned for the project. The quality assurance officer will not be involved in the project data generation process but is responsible for reviewing the SAP and data generating process to ensure that the work be conducted in accordance with the requirements presented in the SAP and to certify that the data is collected and analyzed using the appropriate procedures. The QAO, or designated team, is responsible for preparing and revising the SAP.

Field Analyst

If field analysis is planned, a qualified field analyst will be assigned to conduct the field analysis. A field analyst must have the following minimum qualifications: (1) completion of a certification course or training by an experienced analyst who has demonstrated proficiency in the method; or, (2) demonstration of the analyst's proficiency by correlation of the analyst's results with laboratory confirmation analysis.

Field Team Leader

The field team leader is an experienced person who has demonstrated proficiency in the sampling method. The field team leader is responsible for ensuring that calibration is completed daily in accordance with this procedure, that equipment and instrument inspection and maintenance is conducted, that measurements are taken to the specified accuracy, and that the requisite QA/QC samples are submitted to the laboratory.

Field Sampling Team

Field sampling team is responsible for sampling preparation, sample collection, sample storage at field, sample packaging, sample delivery, and field measurements. The team should be familiar with the SAP.

Project Chemist

The project chemist will have at least two years experience in data review and be familiar with USEPA Region 2 organic data validation requirements and the New York ASP. The project chemist is responsible for data verification, data validation, and data usability evaluation for all analytical data generated for the project.

The project chemist will be responsible for communicating with the laboratory on a regular basis regarding sample shipment, receipt, and login, and all issues relating to data quality, scheduling and data packages. The project chemist will review all project and laboratory documentation related to the analytical process and will prepare data verification reports as needed.

Data Users

Technical personnel who use the collected data to perform their responsibilities (e.g., risk assessment, remedial design) will use the data for various purposes. Data users are responsible for communicating additional data needs to the project manager.

Project Health and Safety Officer

Project health and safety officer oversees the health and safety of personnel involved in the project. Project Health and Safety Officer is responsible for developing the Health and Safety Plan for the project and has the authority to initiate a work stoppage due to health and safety concerns.

3.2.6 Subcontractor

Laboratory

The laboratories selected to perform analyses for samples collected at Seneca site must be certified under the Environmental Laboratory Approval Program (ELAP), implemented by the New York State Department of Health (NYSDOH), and be capable of providing complete environmental analytical services consistent with USEPA protocols and NYSDEC ASP. The laboratories should implement QA/QC procedures consistent with the NYSDEC ASP protocol, Region 2 SOPs, and this generic SAP. Prior to sample analysis, each laboratory must submit detailed information regarding the ELAP certification, laboratory project manager, and QA/QC procedures to Parsons. Parsons Quality Assurance (QA) officer or project chemist will review the ELAP certification and QA/QC manual submitted by laboratories to ensure consistency with requirements by this SAP.

All analytical data will be verified prior to being released by the Laboratory. Verification will include both editorial and technical reviews. The electronic format of the data will be reviewed along with the hardcopy data package. A final review of the data package will be performed and the approved data package signed by the project manager, or designee, when complete.

Other Subcontractors

Other subcontractors identified for specific project will be specified in the SS-WP. The following provides a list of potential subcontractors that may be used for the project.

General Contractors

Abscope Environmental, Inc. (Canastota, New York).
Sessler Wrecking, Inc. (Waterloo, New York)
AAA Environmental (Syracuse, New York)
Maxim Construction (East Syracuse, New York)

Drilling

Nothnagle Drilling (Scottsville, New York).
Northstar Drilling (Homer, New York)
SJB Services, Inc. (Hamburg, New York)
American Auger & Ditching (Constantia, New York)

Surveys

Naybor Surveying (Alden, New York).

3.3 COMMUNICATION PATHWAYS

Communication is one of the keys to a successful project. Communication pathways and modes of communication are delineated in Table 2.

The Laboratory shall communicate with Parsons project manager, QA officer, or project chemist by telephone or via email as necessary throughout the process of sample scheduling, shipment, analysis and data reporting, to ensure that samples are properly processed. This shall include immediately notifying Parsons of any irregularities with samples or sample paperwork received, noting discrepancies between paperwork and verbal orders placed by Parsons authorized personnel, problems encountered in sample analyses that could affect data quality or schedule, and any laboratory conditions that may impact the timeliness of analyses or data reporting. In particular, the Laboratory shall notify Parsons in advance regarding any data that could potentially be late and shall specify an estimated delivery date.

The field team leader shall communicate with the project manager or QA officer by telephone as necessary throughout the sampling event to ensure that samples are properly collected and delivered.

4.0 DATA QUALITY OBJECTIVES

Data Quality Objectives (DQOs) define the type, quantity, and quality of data that are needed to answer specific environmental questions and support environmental decisions. The development of DQOs for a specific site and measurement takes into account project needs, data uses and types and needs, and data collection. These factors determine whether the quality and quantity of data are adequate for its end use. DQOs are implemented so the data are legally and scientifically defensible. This section presents the general process of DQO development and factors that will affect DQO development (Sections 4.1 and 4.2). Site-specific DQOs will be defined in the SS-WP. As part of the DQO development, data performance criteria need to be determined. Section 4.3 presents indicators that will be used to represent data quality and their performance requirement criteria. Section 4.4 describes method detection limits, reporting limits and instrument calibration limits. Section 4.5 and Section 4.6 describe quality control activities and quality control checks for the project, which will be conduced to ensure the data quality.

4.1 DATA QUALITY OBJECTIVE DEVELOPMENT PROCESS

Development of data quality objectives will be conducted in accordance with the USEPA (2000a, c) Guidance for the data quality objectives process, the USEPA (2005a) Uniform Federal Policy for Quality Assurance Project Plans, and the NYSDEC (2001) Development and Review of Site Analytical Plans.

The following elements will be incorporated into the DQO development in accordance with the NYSDEC guidance and the sections corresponding to the elements are specified:

- definition of data types and data uses (Section 4.2),
- specification of data performance criteria (Section 4.3),
- discussion of implementation mechanisms of sampling for routine, baseline and expanded parameters (Sections 4.4 and 4.5)
- presentation of action levels or applicable standards (Section 2.4)

A Systematic Planning Process (SPP) described in the USEPA (2005a) guidance or the Data Quality Objectives Process (DQOP) discussed in the USEPA (2000a, c) guidance will be used to identify site-specific DQOs based on the specific site information.

The SPP process, presented in Figure 13 of the USEPA (2005a) guidance, is based on the scientific method and includes concepts such as objectivity of approach and acceptability of results. It uses a common sense graded approach to ensure that the level of detail in planning is commensurate with the importance and intended purpose of the work and the use of available resources. This framework

promotes communication between all organizations and individuals involved in an environmental project.

When critical environmental decisions need to be made (e.g., final decision-making or compliance with a standard), the USEPA (2000a) defined DQOP will be followed. The DQOP requires statistical expertise to define the amount of error acceptable when making an environmental decision and includes the following seven steps:

- Step 1: State the problem
- Step 2: Identify the decision
- Step 3: Identify the inputs to the decision
- Step 4: Define the boundaries of the study
- Step 5: Develop a decision rule
- Step 6: Specify tolerable limits on decision errors
- Step 7: Optimize the design for obtaining data

The DQO process is iterative, i.e., the seven-step process should be repeated, as needed, based on newly acquired data and/or information.

DQO for a specific project will be presented in a SS-WP. In general, the DQO will be developed using the SPP or DQOP for the Data Quality Objectives Process. Most projects under the contract will be judgmental-based and therefore SPP, a less iterative process, is normally used to develop the project's data quality criteria.

4.2 DATA TYPES AND DATA USES

DQOs are based on the premise that different data types or different data uses require different levels of data quality. This section provides information on potential data type (Section 4.2.1) and data uses (Section 4.2.2) for the project.

4.2.1 Data Types

Two types of data will be produced for the Seneca Depot Activity. Screening data are data generated by rapid methods of analysis with less rigorous sample preparation, calibration and/or QC requirements. Physical test methods (e.g., dissolved oxygen (DO) measurements, temperature, pH, moisture content, turbidity, conductance, etc.) have been designated by definition as screening methods. Screening data are to be used for screening purposes. A summary of screening methods are presented in Table 3.

Definitive data are analytical data that are suitable for final decision-making. All definitive data will be generated using rigorous analytical methods such as approved USEPA SW-846 reference methods. A summary of definitive methods are presented in Table 4. Tables 5-A and 5-B present sample containers, preservatives, and holding times for soils/sediment and aqueous samples, respectively. Table 6-A through Table 6-N present target analyte list for various analytical methods and Table 7-A through Table 7-G present quality control requirements for various analytical methods.

In addition to the above referenced two types of data, nonmeasurement data acquisition may be required for each project. The data that may be required include:

- Climate,
- Geology and soils,
- Hydrogeology,
- Local relevant habitats, and
- Threatened and endangered species.

4.2.2 Data Uses

Data produced under the project will be used by various users for a variety of purposes, such as determining the nature and extent of contamination at a hazardous waste site, assessing priorities for response based on risks to human health and the environment, determining appropriate cleanup actions, determining when remedial actions are complete, and determining compliance with regulatory permit limits and environmental standards. The data may be used in all stages in the investigation of a SWMU, including site inspections, RI/FS, remedial design, treatability studies, and removal actions. In addition, the data may be used in enforcement/litigation activities.

4.3 DATA QUALITY INDICATORS

This section presents a brief introduction of the data quality indicators (DQIs) including precision, accuracy, representativeness, completeness, comparability, sensitivity, and defensibility. The quantitation method for each indicator is discussed in this section. The measurement performance criteria for each indicator identified for the project is presented in Table 7-A through Table 12.

4.3.1 Precision

Precision is a measure of mutual agreement among individual measurements of the same property, usually under prescribed conditions. Assessing precision measures the random error component of the data collection process. Precision is determined by measuring the agreement among individual measurements of the same property, under similar conditions, and is calculated as an absolute value.

The degree of agreement, expressed as the relative percent difference (RPD), is calculated using the formula below.

$$\text{RPD} = \frac{(V_1 - V_2)}{\frac{(V_1 + V_2)}{2}} \times 100$$

where: V1 = value 1; V2 = value 2

Analytical precision can be assessed by analyzing matrix spike/matrix spike duplicate pairs, laboratory control spike (LCS)/laboratory control spike duplicate pairs, and laboratory analytical duplicate samples. Field precision is assessed by measurement of field duplicate samples. The objective for precision is to be within the established control limits for the methods. A note will be provided if RPD is not calculated due to missing data values, "less than" or "greater than" values, or other reasons. The control limits for precision are presented in Table 7-A through Table 7-G, Table 10-A through Table 10-E, and Table 12 and any exceedance of the values listed in the table will trigger corrective actions as presented in Section 11.

4.3.2 Accuracy/Bias

Accuracy is the degree of agreement of a measurement with an accepted reference or true value; bias indicates the systematic or persistent distortion of a measurement process that causes errors in one direction. The terms accuracy and bias are used interchangeably in this document. Accuracy measures the bias or systematic error of the entire data collection process. Sources of these errors include the sampling process, field and laboratory contamination, sample preservation and handling, sample matrix interferences, sample preparation methods, and calibration and analytical procedures. To determine accuracy, a reference material of known concentration is analyzed or a sample which has been spiked with a known concentration is reanalyzed. Accuracy is expressed as a percent recovery and is calculated using the following formula:

$$\%\ \text{Recovery} = 100 \times \frac{\text{measured value}}{\text{true value}}$$

Recoveries are assessed to determine method efficiency and matrix interference effects. Analytical accuracy is measured by the analysis of calibration checks, system blanks, quality control samples, surrogate spikes, matrix spikes, and other checks required by the selected analytical methods. Sampling accuracy is assessed by evaluating the results of field and trip blanks. Sampling accuracy is also maintained by frequent and thorough review of field procedures. The objective of accuracy is to meet the established control limits for the methods. A note will be provided if % recovery is not

calculated due to missing data values, “less than” or “greater than” values, or other reasons. The control limits for precision are presented in Table 7-A through Table 7-G and Table 10-A through Table 10-E and any exceedance of the values listed in the table will trigger corrective action requirements as presented in Section 11.

4.3.3 Representativeness

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is achieved through proper development of the field sampling program. The sampling program must be designed so that the samples collected are as representative as possible of the medium being sampled and that a sufficient number of samples will be collected.

4.3.4 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Data are complete and valid if they meet all acceptance criteria including accuracy, precision, and any other criteria specified by the particular analytical method being used. Data with minor exceedances in accuracy and precision may be considered usable based on a data usability assessment, which is presented in Section 8.7.

Field completeness will be estimated as the percentage of all planned samples that were actually collected and analyzed. The calculation is as follows:

$$\% FC = (A/P) \times 100$$

where,

%FC = Field Percent Completeness;

A = Actual number of samples collected; and

P = Number of planned samples to collect.

Laboratory completeness will be estimated as the percentage of all usable measurements and calculated as follows:

$$\%C = (U/T) \times 100$$

where:

%C = Percent completeness;

U = Number of measurements judged usable; and

T = Total number of measurements.

The objective is to generate a sufficient database with which to make informed decisions. To help meet the completeness objective, every effort must be made to avoid sample loss through accidents or inadvertence. The required completeness for a project will be defined by the SS-WP.

4.3.5 Comparability

Comparability expresses the confidence with which one data set can be compared to another. Comparability must be considered in designing the sampling program and the objective will be met by using standard methods for sampling and analyses specified in this report and by following techniques and methods set forth in the SS-WP.

Whenever definitive analysis is performed to confirm screening results, comparability criteria must be established and documented in the SS-WP prior to data collection. Comparability criteria must be determined for each matrix, analytical group (and analyte, if applicable), and concentration level.

4.3.6 Sensitivity and Quantitation limits

Sensitivity is the ability of the method or instrument to detect the target analytes at the level of interest. Method and instrument sensitivity is measured by developing Method Detection Limits (MDLs) for each analyte of interest. The MDL is a statistically derived value that represents the lowest concentration of an analyte that can be detected with 99 percent confidence that the analyte concentration is greater than zero. And MDL study is performed for each analyte, instrument and matrix and represents the lowest concentration detectable under those conditions.

The quantitation limit (QL) is the minimum concentration of an analyte that can be routinely identified and quantified by a laboratory. The QL is usually three to five times the MDL. For multipoint calibrations, the lowest point of the calibration curve should be at or below the QL. For one-point calibrations, the laboratory should analyze a check standard that contains all target analytes at or below the QL as proof that the analyte can be quantitated at that level.

4.3.7 Defensibility

Data defensibility is defined as data that are both relevant and reliable. This generic SAP was designed to ensure data defensibility for the project. A few key elements that will ensure data defensibility are:

- Appropriate documentation, including Chain of Custody (COC) forms, project records, and analytical traceability
- Using appropriate and approved analytical methodology
- Using NYSDOH ELAP-certified laboratories
- Appropriate sampling design, sample collection, sample handling, and sample storage
- Data validation
- Audits

4.4 METHOD DETECTION LIMITS, REPORTING LIMITS, AND INSTRUMENT CALIBRATION REQUIREMENTS

This section describes the terminology for method detection limit, sample quantitation limit (SQL), and reporting limit (RL) and procedures for MDL and RL studies.

4.4.1 Method Detection Limit Study

The MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence when the analyte concentration is greater than zero. The MDL is lower than the concentration at which the laboratory can quantitatively report. Laboratories determine their "best case" sensitivity for analytical methods by performing MDL studies. The MDL determinations are required at initial analytical method set-up. After the initial study, the MDL determinations shall be performed once per 12 month period, or otherwise be replaced by quarterly MDL verification, as discussed in the following section. In addition, the MDL studies shall be conducted when a major change to the analytical method, instrumentation, or preparation (e.g., extraction) procedure occurs. The MDL study shall be conducted by following the procedure as described in 40 CFR 136 Appendix B. The MDLs achieved by the chosen laboratory within one year prior to the analysis of project samples should be less than or equal to one-half the sample reporting limits.

4.4.2 Method Detection Limit Verification

An MDL verification is performed on an MDL check sample spiked at approximately 2 times the reported MDL to confirm the MDL or to extend the use period of the MDL. The MDL verification can be performed on each instrument immediately following an MDL study to validate the MDL. In addition, after the initial MDL study, the MDL verification can be performed quarterly in lieu of the

annual MDL study. The MDL verification sample shall be taken through all the preparatory and determinative steps used to establish the MDL values. The MDL is verified if the laboratory can reliably detect and identify all analytes in the check sample by the method-specified criteria. If the method has no confirmation criteria, the check sample must produce a signal that is at least 3 times the instrument's noise level. If the MDL is not verified, one of the following three measures should be implemented by the laboratory:

- determine the cause(s) of the verification failure, correct the problem, and repeat the MDL verification.
- spike the MDL check sample at successively higher concentrations until the verification criteria are met, and use the first successful concentration as the reported MDL. The laboratory and project chemist shall ensure the newly established MDL still meets the PQOs.
- reconduct the MDL study.

4.4.3 Sample Quantitation Limit

Frequently, QLs for specific samples are adjusted for dilutions, changes to sample volume/size and extract/digestate volumes, percentage of solids, and cleanup procedures. These QLs are referred to as SQLs.

4.4.4 Reporting Limit

The laboratory participating in any project under this contract shall compare the results of the MDL demonstrations to the RL for each analyte. Laboratory RLs should be at least 3 times the achievable laboratory MDL and ideally 10 times the achievable laboratory MDL. The laboratory shall also verify RL by including a standard at or below the RL as the lowest point on the calibration curve. All results shall be reported at or above the MDL values; however, for those results falling between the MDL and the RL, a laboratory validation flag shall be applied to indicate the analyte was detected, but the concentration is an estimation. No results shall be reported below the MDL. The RL must be at or below the project required RLs specified in the SS-WP.

4.4.5 Project Required Reporting Limit

The project required RL for a target analyte is the numerical value identified for the project. It may be an ARAR or TBC identified for the project such as maximum contaminant levels (MCLs), a risk-based concentration level, a reference-based standard, or a technological limitation. Some commonly used ARARs, TBCs, and other benchmark values are listed in Tables 1-A, 1-B, and Table 6-A through Table 6-N. Project required reporting limit will be specified in the SS-WP based on the specific site condition. Environmental decision-making may be adversely affected by the failure to

meet project required reporting limits. Therefore, laboratory RLs must be less than the project required RLs.

Because of uncertainty at the quantitation limit, project SQLs should be no greater than one-third of the project required reporting limit and ideally one-tenth of the project required reporting limit.

4.4.6 Contract Required Quantitation Limit (CRQL)

CRQL is the minimum level of reliable quantitation acceptable under the USEPA Contract Laboratory Program (CLP). The contract Statement of Work (SOW) for the CLP gives CRQLs, and they are used for RLs (after adjustment for %moisture and dilution). The CLP CRQLs are set at the concentration of the lowest non-zero standard in the calibration curve. Organic analytes that are positively identified below the CLP CRQL are reported as present, but at an estimated concentration (with a "J" flag). The laboratory RL should be reported below the CRQL under the CLP program. Inorganic analytes reported at a concentration above the laboratory's RLs but below the CLP CRQL are flagged with a "B".

4.4.7 Instrument Calibration

Measuring and testing instrument shall have an initial calibration and shall be recalibrated/verified at scheduled intervals against certified standards that have known and valid traceability to recognized national standards. Calibration intervals for each item shall be, at a minimum, in accordance with manufacturer's recommendations as defined in the instrument manual, the analytical method, the NYSDEC ASP, and the project specific QA requirements.

Calibration standards shall be maintained and used in an environment with temperature, humidity, and cleanliness controls that are compatible with the accuracy and operating characteristics of the standards. An inspection will be made during the instrument calibration to evaluate the physical condition of the instrument. The purpose of the inspection is to detect any abnormal wear or damage that may affect the operation of the instrument before the next calibration. Instrument found to be out of calibration or in need of maintenance or repair will be identified and removed from service.

The laboratory QA Officer shall be notified if the instrument is found to be out of tolerance during inspection and calibration. The corrective actions to be taken include evaluating the validity of previous inspection or test results; evaluating the acceptability of the items inspected or tested since the last calibration check; and repeating the original inspections or tests using calibrated instrument when it is necessary to establish the acceptability of previous inspections or tests. Specifics regarding QC checks and verification of equipment stability are presented in Table 7-A through 7-G for laboratory instrument and Table 11 for field instrument.

All measuring and testing instrument use shall have current documentation of the calibration status and calibration expiration date. Instrument history records for measurement and test equipment shall be used to indicate calibration status and conditions, corrections to be applied, results of in-service checks, and repair history. This will provide a basis for establishing calibration frequencies and for remedial action if the instrument is found out of calibration.

4.4.7.1 Laboratory Instrument Calibration

Analytical instruments shall be calibrated in accordance with the analytical methods. All target analytes reported shall be present in the initial and continuing calibrations, and these calibrations shall meet the acceptance criteria specified in Table 7-A through Table 7-G. All results reported shall be within the calibration range. Results outside the calibration range are unsuitable for quantitative work and only give an estimate of the true concentration. For SW6010 and SW6020, results shall be within the working linear range determined by linear range studies performed in accordance with the method and NYSDEC ASP. Records of standard preparation and instrument calibration shall be maintained.

Records shall unambiguously trace the preparation of standards and their use in calibration and quantitation of sample results. Calibration standards shall be traceable to standard materials. Instrument calibration shall be checked using all target analytes identified in the project-specific requirements and surrogates. If no project-specific analytes are identified, the analytes listed in Table 6-A through Table 6-N shall serve as the default analytes for the method.

This applies equally to multicomponent analytes (e.g., PCBs). All calibration criteria shall satisfy NYSDCE ASP at a minimum. The initial calibration (ICAL) must be verified by a second source standard. Multipoint calibrations shall contain the minimum number of calibration points specified in Table 7-A through Table 7-G with all points used for the calibration being contiguous. If more than the minimum number of standards is analyzed for the ICAL, all of the standards analyzed shall be included in the ICAL. The only exception to this rule is a standard at either end of the calibration curve can be dropped from the calibration, providing the requirement for the minimum number of standards is met.

Acceptance criteria for the calibration are presented in Table 7-A through Table 7-G. Analyte concentrations are determined with either calibration curves or response factors (RFs). For gas chromatography (GC) and GC/mass spectrometry (GC/MS) methods, when using RFs to determine analyte concentrations, the average RF from the ICAL shall be used. The continuing calibration shall not be used to update the RFs from the ICAL. The continuing calibration verification (CCV) cannot be used as the LCS, except for methods that do not involve sample preparation (e.g., volatile organic analysis). A CCV is to be performed daily before sample analysis (unless an ICAL and second-source standard verification is performed immediately before sample analysis) and as required by the applicable method and the SAP (Table 7-A through 7-G gives the appropriate frequencies.). In

addition, the concentration used for the CCV sample shall be at or below the middle of the calibration curve. Finally, the lowest standard used must be at or below the RL for each analyte in the method.

If calibration acceptance criteria are not met, corrective action will be implemented and recalibration conducted, and the laboratory will reanalyze all samples since last successful calibration verification.

4.4.7.2 Field Instrument Calibration

The frequency of calibration for field instruments will be performed at the intervals specified by the manufacturer or more frequently as conditions dictate, but daily as a minimum. To ensure comparability between sample data of similar samples and sample conditions, standard solutions and material traceable to the National Institute of Standards and Technology (NIST) or USEPA-published standards/protocols will be used to calibrate the field instruments. Table 11 summarizes requirement for field equipment calibration, maintenance, testing, and inspection.

4.5 QUALITY CONTROL ACTIVITIES

QC elements relevant to screening data are presented in Section 6.0. This section presents QC requirements relevant to analysis of environmental samples that shall be followed during all analytical activities for fixed-base, mobile, and field laboratories producing definitive data. The purpose of these QC activities is to produce data of known quality that satisfy the project quality objectives (PQOs). These activities provide a mechanism for ongoing control and evaluation of data quality measurements through the use of QC materials.

Laboratory quality control samples (e.g., method blanks and LCS samples) shall be included in each preparation batch with the field samples. A project analytical batch (PAB) is a group of samples (not exceeding 20 environmental samples plus associated laboratory QC samples) that are similar in composition (matrix) which are extracted or digested at the same time and with the same lot of reagents and analyzed together as a group. The term “PAB” also extends to cover samples that do not need separate extraction or digestion (e.g., volatile analyses by purge and trap). The laboratory shall determine optimum batch size by the number of samples of similar matrix with the ability to be processed simultaneously through the entire preparation and analytical process within a normal work shift. In order to preserve the integrity of the sample designation, it is required whenever possible that all samples received on a given date be prepared and analyzed in the same PAB. The identity of each PAB shall be unambiguously reported with the analyses so that a reviewer can identify the QC samples and the associated environmental samples. All references to the analytical batch in the following sections and tables in this SAP refer to the PAB.

The following sections summarize quality control activities for the Seneca Army Depot Activity including laboratory selection requirement and QC sample requirement. Table 13 presents a

summary of QC sample types and general requirements for QC samples. Frequency of project QA/QC sample collection and requirements, if varied from this generic SAP, will be specified in the SS-WP.

4.5.1 Laboratory Certification, Qualification, and Selection

To be selected for project chemical analysis, the laboratory should be certified by the NYSDOH ELAP program. The following four laboratories have been identified as potential laboratories for the project.

1) Severn Trent Laboratories, Inc.
   Tel: (617) 901-7306
   Contact: Rick Carr

   Severn Trent Laboratories, Inc. (STL Pittsburgh)
   301 Alpha Drive
   Pittsburgh, PA 15238
   Tel: 412-963-7058
   Contact: Mr. David Miller

   Severn Trent Laboratories, Inc. (STL Buffalo)
   10 Hazelwood Drive, Suite 106
   Amherst, NY 14228
   Tel: 716-691-2600
   Contact: Tony Bogolin

2) Columbia Analytical Services
   1 Mustard St., Suite 250
   Rochester, NY
   Tel: (585) 288-5380
   Contact: Mike Perry/Mark Wilson

3) AmeriSci Boston
   8 School Street
   East Weymouth, MA 02189
   Tel: 781-337-9334
   Contact: Bud Gibson

For each specific project, the project team will identify appropriate laboratory that conforms to the requirements presented in this SAP. In brief, the laboratory should follow the requirements presented below:

- For the analysis of any aqueous samples for a parameter or category of parameters for which laboratory certification exists pursuant to NYSDOH ELAP Certification, the laboratory should be certified for that specific parameter or category of parameters pursuant to NYSDOH ELAP Certification;
- For the analysis of non-aqueous samples using specific analytical methods contained in the USEPA Publication SW-846, "Test Methods for Evaluating Solid Waste", third edition, update IIF, January 1995, as amended and supplemented, for a parameter or category of parameters for which certification exists pursuant to NYSDOH ELAP Certification, the laboratory will be certified for that specific parameter or category of parameters pursuant to NYSDOH ELAP Certification or, at a minimum, have obtained temporary approval to analyze regulatory samples pursuant to NYSDOH ELAP Certification;
- The reporting limits for chemicals of potential concern should be within the limits specified in the SAP or SS-WP;
- The laboratory should follow the QA/QC procedures described in the NYSDEC ASP;
- The laboratory should report the analytical results consistent with the NYSDEC ASP requirement and those specified in the SAP (Section 8.2.1);
- The laboratory shall provide an electronic data deliverable (EDD) in accordance with the NYSDEC ASP requirement (Exhibit H) and the requirements presented in Section 8.

The laboratory identified for the project will be specified in the plans-WP.

4.5.2 Sample Receipt Requirements

The laboratory shall comply with the following specifications for sample receipt:

- The laboratory shall sign air bills upon receipt and keep copies in the project file.
- Shipping container custody seals shall be inspected and the condition documented.
- Condition of the samples shall be documented in the Cooler Receipt and Inspection Form with signature and date of person checking samples. This form will be included with the hardcopy report.
- The pH of preserved samples shall be checked with pH paper upon receipt and documented.
- Any breakage, discrepancy, or improper preservation shall be noted by the laboratory as an out-of-control event and shall be documented on the Cooler Receipt and Inspection Form with the corrective action taken. The Cooler Receipt and Inspection Form shall be signed and dated by the

custodian or the project manager of the laboratory. The laboratory project manager shall notify Parsons of discrepancies and any noncompliant issues in shipments within 24 hours of sample receiving. Sample log-in information shall be emailed or faxed to Parsons Project QA Manager or project chemist within 24 hours of sample receiving. Sample log-in information shall be emailed or faxed to Parsons project chemist within 28 hours of sample receipt.

4.5.3 Laboratory Control Sample (LCS)

The LCS is a blank matrix (contaminant-free water or an inert solid such as glass beads or Teflon® chips) that is spiked with a known concentration of all target analytes. Each analyte in the LCS shall be spiked at a level less than or equal to the midpoint of the calibration curve (The midpoint is defined as the median point in the curve, not the middle of the range).

The LCS shall be carried through the complete sample preparation and analysis procedure. At least one LCS shall be included in every PAB. If more than one LCS is analyzed in a single PAB, results from all LCS samples shall be reported. The failure of any analyte in the LCS shall require appropriate corrective action, including possible qualification of the failed analyte in all associated samples.

4.5.3.1 LCS Control Limits

The LCS control limits are presented in Table 7-A through Table 7-G and Table 9-A through Table 9-G. The limits are based on those specified in the NYSDEC ASP and the USEPA Region 2 SOPs. The laboratory may use in-house LCS control limits. However, those limits must be within the LCS control limits listed in the tables, if applicable. The performance of the LCS is evaluated against the control limits. When an analyte in the LCS exceeds the upper or lower control limit and no corrective action is performed or the corrective action is ineffective, the appropriate flag, consistent with the USEPA Region 2 SOPs, shall be applied to all affected results. Once an LCS has failed (as specified in Table 7-A through Table 7-G), corrective action is required.

4.5.3.2 LCS Corrective Action

If a sample fails based on the criteria presented in Table 7-A through Table 7-G, corrective action is required. The corrective action requirement applies to all analytes that exceeded the LCS control limits, even if one specific analyte's exceedance was not the trigger of LCS failure.

If an LCS fails, an attempt must be made to determine the source of error and find a solution. All the findings and corrective action should be documented. If a systematic problem is found, the problem should be resolved and system control reestablished. Following the reestablishment of control, all samples in the PAB shall be re-prepared and reanalyzed for the out-of-control analyte(s). The

corrective action applied shall be based on professional judgment in the review of other QC measures (i.e., surrogates). If an analyte falls outside the LCS control limits a second time or if there is not sufficient sample material available to be reanalyzed, then all the results in the PAB for that analyte will be flagged in accordance with the USEPA Region 2 SOPs. The recoveries of those analytes subject to corrective action must be documented in the case narrative, whether flagging is needed or not.

4.5.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) and matrix spike duplicate (MSD) is an aliquot of sample spiked with known concentrations of all target analytes. The spiking occurs prior to sample preparation and analysis. Each analyte in the MS and MSD shall be spiked at a level less than or equal to the midpoint of the calibration curve for each analyte. Only project samples shall be used for spiking. The MS/MSD shall be designated on the chain of custody. MS and MSDs are treated as environmental samples.

The MS/MSD pair is used to document potential matrix effects associated with a site. Parsons project managers must select the samples for MS/MSD analysis. The sample replicates will be collected in the field and will be used by the laboratory to prepare and analyze the appropriate MS/MSDs. Only one soil sample container may be necessary for the parent sample, the MS sample, and the MSD sample with the exception of volatile organic analysis (VOA).

A site-specific MS/MSD should be specified for each media (e.g., any different soil, water, or sediment) at each site during each sampling event. Project managers should designate the MS/MSD and determine whether they are site specific based on the project requirements. A minimum of one MS and one MSD shall be designated by the project manager for each site and included for every 20 field samples (i.e., collect up to 20 field samples followed by two additional samples designated as MS and MSD). More than one MS/MSD pair may be submitted as part of the sample group of environmental samples; however, project managers must coordinate with the laboratory providing analytical services for most cost effective sampling. Based on the projects size and duration, it is possible that not every sample delivery group will include an MS/MSD pair. This is acceptable provided the overall project requirements are met.

The performance of the MS and MSD is evaluated against the QC acceptance limits given in Table 7-A through 7-G and Table 10-A through 10-E. If either the MS or the MSD is outside the QC acceptance limits, the data shall be evaluated to determine whether there is a matrix effect or analytical error and whether the analytes in all related samples shall be qualified according to the USEPA Region 2 SOPs. The laboratory should communicate potential matrix difficulties to Parsons so an evaluation can be made with respect to the PQOs.

4.5.5 Surrogates

Surrogates are compounds similar to the target analyte(s) in chemical composition and behavior in the analytical process but not normally found in environmental samples.

Surrogates are used to evaluate accuracy, method performance, and extraction efficiency. Surrogates shall be added to all environmental samples, controls, and blanks, in accordance with the method requirements.

Whenever a surrogate recovery is outside the limits presented in Table 8 or required by the method, corrective action must be performed. If systematic problems are found, the problems should be resolved and system control reestablished. After the reestablishment of control, the affected sample(s) should be re-prepared and reanalyzed. If corrective actions are not performed or are ineffective, or if sufficient sample volume is not available for reanalysis, the appropriate flag, consistent with the USEPA Region 2 SOPs, shall be applied to the sample results. Table 7-A through Table 7-G present corrective action and flagging criteria for various methods..

4.5.6 Internal Standards (IS)

ISs are known amounts of standards added to a portion of a sample or sample extract and carried through the entire determination procedure. They are used as a reference for calibration and for controlling the precision and bias of the analytical method.

ISs shall be added to all environmental samples, controls, and blanks, in accordance with the method requirements.

When the IS results are outside of the acceptance limits, corrective actions shall be performed. If systematic problems are found, the problems should be resolved and system control reestablished. After the reestablishment of control, the affected sample(s) should be re-prepared and reanalyzed. If corrective actions are not performed or are ineffective, or if sufficient sample volume is not available for reanalysis, the appropriate flag, in accordance with the USEPA Region 2 SOPs, shall be applied to the sample results.

4.5.7 Retention Time (RT) Windows

RT windows are used in GC, ion chromatography (IC) and high performance liquid chromatography (HPLC) analysis for qualitative identification of analytes. They are calculated from replicate analyses of a standard performed on multiple days. The procedure and calculation method are given in SW-846, Method 8000C. The center of RT window is established for each analyte and surrogate using the RT of the mid-point standard of the ICAL. For non-MS methods, the RTs for each analyte are

updated daily using the absolute RTs from the calibration verification performed at the beginning of each PAB.

If a significant shift in RTs is observed, the analyses should be halted and the instrumentation should be inspected to identify the cause of the shift. After any systematic problems have been resolved and system control has been reestablished, reanalyze all samples run after the shift occurred. If corrective actions are not performed, the appropriate flag, in accordance with the Region 2 SOPs, shall be applied to the sample results.

4.5.8 Interference Check Samples (ICSs)

ICSs are used in inductively coupled plasma-atomic emission spectra (ICP-AES) and Inductively Coupled Plasma-Mass Spectra (ICP-MS) analyses only and contain known concentrations of both interfering and analyte elements.

The ICSs are used to verify background and interelement correction factors.

The ICSs are run at the beginning of each run sequence for SW6010B and SW6020B.

When the ICS results are outside of the acceptance limits given in Table 7-C and Table 7-D, corrective action shall be performed. After the system problems have been resolved and system control has been reestablished, reanalyze the ICSs. If the ICS results are acceptable, reanalyze all affected samples. If corrective action is not performed or the corrective action was ineffective, the appropriate flag, in accordance with the USEPA Region 2 SOPs, shall be applied to all affected results.

4.5.9 Method Blank

A method blank is an analyte-free matrix carried through the complete sample preparation and analytical procedure. The method blank is used to assess possible contamination resulting from the preparation or analytical process. A method blank shall be included in every PAB.

The presence of analytes in a method blank at concentrations greater than the MDL indicates the need for further assessment of the data. The source of contamination should be investigated and measures must be taken to correct, minimize, or eliminate the problem if the concentration exceeds the RL or CRQL. For common laboratory contaminants (e.g., methylene chloride, acetone, phthalates), the concentration found in the method blank must not exceed the limits specified in Table 7-A through 7-G. No analytical data shall be corrected for the presence of analytes in blanks. When an analyte is detected in the method blank and in the associated samples and corrective actions are not performed

or are ineffective, the appropriate flag, as described in the USEPA Region 2 SOPs, shall be applied to the sample results.

4.5.10 Equipment Blank

An equipment blank is a sample of American Society for Testing and Materials (ASTM) Type II reagent grade water poured into or over or pumped through the sampling device, collected in a sample container, and transported to the laboratory for analysis. These may also be called rinse blanks or rinsate blanks.

Equipment blanks are used to assess the effectiveness of equipment decontamination procedures.

Equipment blanks shall be collected immediately after the equipment has been decontaminated and included for each sampling event as appropriate. The equipment blank samples shall be analyzed for all parameters requested for the environmental samples collected at the site. The frequency of collection for equipment blanks will be specified in the SS-WP.

When an analyte is detected in the equipment blank, the appropriate flag, as described in USEPA Region 2 SOPs, shall be applied to all sample results from samples collected with the affected equipment.

4.5.11 Trip Blank

The trip blank consists of a volatile organic compound (VOC) sample vial filled in the laboratory with ASTM Type II reagent grade or organic-free water, transported to the sampling site, handled like an environmental sample and returned to the laboratory for analysis. Trip blanks are not opened in the field. Trip blanks are only submitted when samples are collected and analyzed for VOC analytes.

Trip blanks are used to assess the potential introduction of contaminants from sample containers or during the transportation and storage procedures. At least one trip blank should be prepared for each group of coolers that contain samples for VOC analysis delivered at the same time. In accordance with the USEPA Region 2 (1989) CERCLA Quality Assurance Manual, an aqueous trip blank is not required when non-aqueous samples are collected.

When an analyte is detected in the trip blank and in the associated samples, the appropriate flag, as described in the USEPA Region 2 SOPs, shall be applied to all sample results from samples in the cooler with the affected trip blank.

4.5.12 Field Duplicate (Replicate) Samples

Field duplicates are two (or more) field samples taken at the same time in the same location. They are intended to represent the same population and are taken through all steps of the analytical procedure in an identical manner. These samples are used to assess precision of the entire data collection activity, including sampling, analysis, and site heterogeneity.

Duplicate samples are collected simultaneously or in immediate succession, using identical recovery techniques, and are treated in an identical manner during storage, transportation, and analysis. The samples may be either collocated samples or subsamples (replicates) of a single sample collection. Examples of collocated samples include ambient air monitoring samples, surface water grab samples, and side-by-side soil core samples, while subsamples may be taken from one soil boring or sediment core. The sample containers are assigned a unique identification number in the field. Specific locations should be designated for collection of field duplicate samples prior to the beginning of sample collection.

It is recommended to collect one sample per week or 10% of all field samples per matrix, whichever is greater (USEPA, 2004b). Precision acceptance criteria are given in Table 12.

4.5.13 Laboratory Duplicate Samples

Laboratory duplicate samples, also known as analytical duplicates, demonstrate the precision of the analytical process within the laboratory. A minimum of one analytical duplicate sample shall be performed for every 20 field samples. Acceptance criteria are given in Table 12.

4.6 QUALITY CONTROL CHECKS

This section summarizes quality control checks including sample holding time compliance check, quantitation confirmation for samples analyzed using GC or HPLC, standard material check, and supplies and consumables check.

4.6.1 Holding Time Compliance

To maximize representativeness of sample results, all samples will be extracted and/or analyzed within the holding times specified in each method. Tables 5-A and 5-B present the maximum holding times allowed for each method. Extraction or analysis performed after the expiration of the holding time will result in the qualification of the results during the data validation procedures. The holding time requirement should be applied to all samples including samples diluted for reanalysis and samples reanalyzed due to quality control issues.

Any samples extracted and/or analyzed beyond project required holding time for extraction or analysis may be resampled and resubmitted for analysis.

It should be noted that the NYSDEC ASP requires holding times to be calculated from the verified time of sample receipt (VTSR) and not from the sample collection date and time. Tables 5-A and 5-B list both technical holding time requirement and NYSDEC ASP holding time requirement. The laboratory shall extract and/or analyze each sample within both the technical holding time and NYSDEC ASP holding time requirement presented in Tables 5-A and 5-B.

4.6.2 Quantitation Confirmation

Quantitative confirmation of results at or above the RL for samples analyzed by GC or HPLC shall be required, unless otherwise specified in the SS-WP, and shall be completed within the method-required holding times. If holding times are exceeded and the analyses are performed, the results shall be flagged according to the USEPA Region 2 SOPs. For GC methods, a second column is used for confirmation. For HPLC methods, a second column or a different detector will be used. Unless otherwise specified or overlapping peaks are causing erroneously high results, the lower of the two confirmed results shall be reported as the primary result. The column used for both the primary and confirmation results shall be indicated on the sample reports. The associated calibration and QC results (including method blank, LCS, MS/MSD, surrogates and ISs) shall be submitted for both columns so that sample results can be appropriately evaluated.

4.6.3 Standard Materials

Standard materials, including second source materials, used in calibration and to prepare samples shall be traceable to NIST, USEPA, American Association of Laboratory Accreditation (A2LA) or other equivalent source, if available. If an NIST, USEPA, or A2LA standard material is not available, the standard material proposed for use shall be included in an addendum to the laboratory QA manual submitted to Parsons before the analyses. The standard materials shall be current, and the following expiration policy shall be followed: The expiration dates for standards shall not exceed the manufacturer's expiration date or one year from the date of receipt, whichever comes first. Expiration dates for laboratory prepared stock and diluted standards shall be no later than the expiration date of the stock solution or material or the date calculated from the holding time allowed by the applicable analytical method, whichever comes first. Expiration dates for pure chemicals shall be established by the laboratory and be based on chemical stability, possibility of contamination, and environmental and storage conditions. Expired standard materials shall be either revalidated prior to use or discarded. Revalidation may be performed through assignment of a true value and error window statistically derived from replicate analyses of the material as compared to an unexpired standard. The laboratory shall label standard and QC materials with expiration dates.

A second source standard is used to independently confirm the ICAL. A second source standard is a standard purchased from a vendor different from that supplying the material used in the ICAL. The second source material can be used for the continuing calibration standards and/or for the LCS. Two different lot numbers from the same vendor do not normally constitute a second source. However, when a project requires analyses for which there is not a separate vendor source available, the use of different lot numbers from the same vendor will be acceptable to verify calibration.

4.6.4 Supplies and Consumables

The laboratory shall inspect supplies and consumables prior to their use in analysis. The materials description in the methods of analysis shall be used as a guideline for establishing the acceptance criteria for these materials. Purity of reagents shall be monitored and documented. An inventory and storage system for these materials shall assure use before manufacturers' expiration dates and storage under safe and chemically compatible conditions. As part of the laboratory's maintenance program, service contracts are held on sufficient supplies. SOP's for routine maintenance of supplies and consumables shall be submitted for each laboratory performing analytical services as part of this project. Consistent with the Uniform Federal Policy for Quality Assurance Project Plans, the documentation should include the following:

- Supplies that will be used in the performance of analytical work
- All vendors for supplies and reagents
- Specifications for all supplies and reagents that could affect data quality (such as level of contamination, pesticide versus reagent-grade). Procedures that will be used to ensure supply cleanliness and reagent purity (such as recording reagent lot numbers)
- Procedures for measuring supply cleanliness
- Corrective action procedures for preventing the use of unacceptable supplies

The laboratory shall purchase or prepare sample containers in accordance with the specifications in the NYSDEC ASP (Exhibit I) and the SAP (Table 5-A and Table 5-B), unless specifically directed to do otherwise by Parsons. The individuals responsible for checking supplies and implementing corrective actions will be identified by the laboratory. Laboratory QA manuals, which include supplies and consumables inspection SOP, will be reviewed by Parsons project chemist before the analysis starts.

Supplies and consumables for field activities will be inspected by field team leader. Table 11 presents inspection requirement and Table 14 provides a critical supplies and consumable tracking log.

5.0 SAMPLING PROCEDURES

5.1 FIELD SAMPLING PROCEDURES

Field sampling procedures including field sample collection SOPs and field sample storage are presented in Section 16.

5.2 SAMPLE COLLECTION DOCUMENTATION

Documentation for sample collection includes sample container identification, field notes recording any observation during the sample collection, and the COC discussed in detail in the following section.

The sample label requirement is discussed in detail in Section 16. The information on the label will be preserved by covering the label with clear tape to minimize water damage during transit. Requirement for other field documentation (e.g., field logbooks and field data collection forms) is presented in Section 16.

5.3 SAMPLE HANDLING AND CUSTODY

A sample is physical evidence collected from a facility or from the environment. Controlling evidence is an essential part of the hazardous waste investigation effort. To accomplish this, proper sample handling and custody procedure should be followed. Table 16 illustrates the sample handling system.

5.3.1 Sample Identification

To assure traceability of the samples, samples should be properly labeled in the field with assigned sample identification (ID). The Laboratory shall have a specified method for maintaining identification of samples throughout the Laboratory. Each sample and sample preparation container shall be labeled with the sample identifier. If the sample identifier is different from the sample ID assigned at the field, it shall be cross-referenced to the sample ID.

5.3.2 Sample Handling

The following summarizes the general sample flow:

- Sample collection, packaging, and shipment,
- Sample receipt and analysis,
- Sample archiving, and

- Sample disposal

Table 16 identifies personnel primarily responsible for ensuring proper handling, custody, and storage or field samples during the above different stages of sample flow.

5.3.3 Sample Delivery

Unless specified in the SS-WP, samples will be delivered directly to the laboratory facility by overnight delivery service via common carriers (e.g., Federal Express and United Parcel Service Inc.). Samples will be grouped in sample delivery groups (SDGs) and each SDG should contain 20 or fewer field samples within a project. An SDG signifies a group of samples collected at one site or geographical area over a finite time period, and will include one or more field samples with associated QA/QC samples. Samples may be shipped to the Laboratory in a single shipment or multiple shipments over a period of time, depending on the size of the SDG. A SDG is defined by the following, whichever is most frequent:

- Each cooler of field samples received, or
- Each 20 field samples (including field QC samples) within an SDG, or
- Each 7 calendar day period (excluding Sundays and Government holidays) during which field samples in an SDG are received (said period beginning with the receipt of the first sample in the SDG).

Samples should be packaged, marked and labeled in accordance with the SAP (Section 16). Samples should be shipped in compliance with the most recent U.S. Department of Transportation (DOT) regulations for shipping hazardous and nonhazardous materials, and in accordance with the analytical methodology. Shipment papers, including bills of lading and airbills, should be retained by the laboratory with COC records. COC forms will be used as sample shipment forms.

5.3.4 Sample Custody

Sample custody procedures ensure accountability for the location and integrity of the sample at all times. Sample custody documentation for the project includes COC forms, custody seals provided by the laboratory, laboratory sample receipt forms, laboratory sample transfer forms, traffic reports (e.g., air bills), and sample ID.

A COC record accompanies the sample container from the laboratory to the field where the sample is collected, preserved, and then returned to the laboratory. The field sampling team should neatly and clearly fill out the COC form provided by the laboratory. Special care should be used to differentiate the number zero from the letter “O”, the number five from the letter “S” and the number one from the letter “I”. Each cooler shipped to the laboratory should contain its own COC form. The field

sampling team should file one copy of each COC in the project file, place the remaining copy (or copies) in a zip-top baggie and attach the baggie to the inside lid of the associated cooler. The laboratory's sample custody program must meet the criteria listed below.

- The laboratory has designated a sample custodian who is responsible for maintaining sample custody and for maintaining all associated records documenting sample custody.

- Upon receipt of the samples, the custodian signs the COC record and records the date and time the samples are received. The custodian then measures and records sample temperature (using the temperature blank if available) on a cooler receipt form, checks for proper preservation, and checks the original COC documents and compares them with the labeled contents of each sample container for correctness and traceability. In the event any discrepancy is found, or the cooler temperature is outside the acceptable range of 2 to 4^{o}C, the laboratory should immediately contact Parsons project manager as part of the corrective action process. Parsons project manager will notify the Army if samples are received outside the above listed temperature range.

- A qualitative assessment of each sample container is performed to note any anomalies, such as broken or leaking containers. This assessment will be recorded as part of incoming COC procedures. In the event any sample containers are received compromised, the laboratory should immediately contact the Parsons project manager as part of the corrective action process.

- The samples are stored in a secured refrigerator until analyses begin. Refrigerators will be maintained at 4 °C ± 2 °C, and the temperatures will be recorded daily.

- A copy of the COC and cooler receipt forms should be included in each laboratory data package.

Sampling packaging and shipment SOPs (including types of sample tags, labels, custody seals, and forms to be used, sample numbering system, and other sample handling and tracking information) are presented in Section 16.

5.3.5 Unused Sample and Extracts Storage

All samples should be submitted with more than enough volume for analysis (i.e., at least twice the volume required for analysis) and any remaining sample volume will be appropriately stored by the laboratory. The laboratory is required to retain unused sample volume and used sample containers for a period of 120 days after data submission. From the time of receipt until disposal, the laboratory shall maintain all samples and unused sample volumes at 4°C (±2°C) and protected from light. Samples and unused sample volumes must be stored separately from sample extracts and standards. The laboratory shall retain all sample extracts after analysis in bottles/vials with Teflon®-lined septa

and shall maintain stored extracts at 4°C (±2°C). The laboratory is required to retain the sample extracts for 180 days after data submission.

6.0 SCREENING ANALYTICAL METHODS

Screening or non-definitive analytical methods can be useful tools in generating quality environmental data. These methods should be selected as part of the overall systematic planning process and can serve to minimize sampling error, thereby minimizing costs. The various analytical screening methods that may be used for the project are shown in Table 3. Table 3 also presents a summary of RLs for screening methods. Table 17 summarizes calibration and QC procedures for the screening methods. The methods and QC procedures were taken from *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (USEPA SW-846, Third Edition, and its subsequent updates), *Methods for Chemical Analysis of Water and Waste* (USEPA 1979), *ASTM Annual Book of Standards* (1993), and from various manufacturers' literature. Specific methods for a project are to be selected from Table 3 unless a variance is requested. The list below is not intended to be all inclusive. Other appropriate methods based on site-specific PQOs will be provided in the SS-WP.

Methods acceptable to the NYSDEC will be utilized for the determination of the presence of free product in soil or water. Such method include, without limitation, visual identification of sheens or other visible product, measurable thickness of product on the water table, the use of field instruments, ultraviolet fluorescence, soil-water agitation, centrifuging, and hydrophobic dye testing (NYSDEC, 2002).

Field screening analysis should be conducted consistent with the NYSDEC DER-10, Section 2.1(g). In brief, field screening methods for all sampling matrices (soil, water, air, interior surfaces) can only be used for contaminant delineation if contaminant identity is known or if there is reasonable certainty that a specific contaminant may be present; or to bias sample location to the location of greatest suspected contamination. Field screening methods should not be used to verify contaminant identity or clean zones unless there has been an correlation study approved in advance by the Division of Environmental Remediation (DER) for the specific site where screening methods are proposed for verification. Where field screening is used, a SOP will be developed and a duplicate analysis of 10% of the samples will be conducted. Laboratory confirmation on 10% of the samples by a standard ASP method is required. There should be no bias in the selection of duplicate or LCSs, such as selecting positive detections for duplication or confirmation. The duplicate or confirmation analysis should be done on every 10^{th} sample, selected in the order they are presented for analysis. Laboratory confirmation occurs if the correlation between field screening and laboratory results are within +/- 30%. Analysis must be done by a Field Analyst with the following minimum qualifications: (1) Completion of a certification course or training by an experienced analyst who has demonstrated proficiency in the method; or, (2) Demonstration of the analyst's proficiency by correlation of the analyst's results with laboratory confirmation analysis.

7.0 DEFINITIVE DATA ANALYTICAL METHODS

This section presents sample preparation methods and analytical methods. The identified methods basically follow requirements and guidelines set out in the USEPA SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA Region 2 SOPs, and NYSDEC Analytical Services Protocol (2000). These methods have been developed specifically for the highly variable environmental samples and are reviewed and updated on a frequent basis in order to obtain the best possible quality data. Although specific method updates are noted in this document, the most recent updates to USEPA SW-846 and the NYSDEC ASP should be used if specified in the SS-WP.

As with the screening procedures in Section 6, the following methods and associated quality control requirements are subject to project-specific objectives developed during the DQO or systematic planning process. Once adopted, modification of these method-specific quality control and corrective action requirements involves appropriate communication and demonstration that the variances are adherence to PQOs and are consistent with the USEPA and NYSDEC ASP program goals. The ultimate goal is the generation of the highest quality defensible data necessary for informed decisions affording the decision-makers or stakeholders, a known and documented level of acceptable risk associated with the respective decision(s).

Section 7.1 presents brief description of preparation methods and Section 7.2 contains brief description of analytical methods. Table 6-A through Table 6-N present target analyte lists for various analytical methods and Table 7-A through Table 7-G present quality control requirements for various analytical methods. Table 8 summarizes performance criteria for surrogate recovery, Table 9-A through Table 9-G provides QC limits for LCS, Table 10-A through 10-E specifies QC criteria for MS/MSD results, and Table 12 presents performance criteria for field duplicates and laboratory duplicates.

7.1 SAMPLE PREPARATION METHODS

In accordance with the NYSDEC DER-10 guidance, sample matrix cleanup methods will be performed if:

1. Petroleum contaminated soils, sediments, or other solids are analyzed for semivolatile organics (SVOCs), and the MDLs are elevated above the applicable remediation standard because of matrix interference;

2. GC peaks are not adequately separated due to matrix interference. A peak will be considered inadequately separated when a rise in baseline or extraneous peaks interfere with:

- the instrumental ability to correctly identify compounds present (including ISs and surrogates), and/or;

- the integration of peak area and subsequent quantitation;

3. So specified by the analytical method; or

4. Matrix interferences prevent accurate quantification and/or identification of target compounds.

7.2 ANALYTICAL METHODS

Analytical methods should be identified based on site-specific information and objective and should be specified in the SS-WP. This SAP has identified several commonly used analytical methods for the project and the corresponding performance criteria are presented in Table 7-A through 7-G. Any variation from the methods identified in this SAP or selection of an appropriate method not recorded in the SW-846 or NYSDEC ASP should be documented in the SS-WP and a SOP should be developed and recorded. For tissue analysis, methods for each analyte to be tested will be proposed and approved by the NYSDEC.

For all petroleum storage and discharge areas, sample analysis should be conducted pursuant to the requirements of Spill Technology and Remediation Series (STARS) Memo #1 - Petroleum-Contaminated Soil Guidance Policy. Samples taken in non-petroleum storage and discharge areas should be analyzed for the stored material. Analysis should be conducted using any GC method by a laboratory that is certified pursuant to NYSDOH ELAP for the category of parameters being analyzed.

7.3 ANALYTICAL SOPS

Table 4 presents a list of analytical methods that will be used for the project. A NYSDEC ASP program, which contains SOPs for the referenced analytical methods, is attached in Appendix B. SOPs for the other analytical methods can be found from various sources.

7.4 TARGET COMPOUND

Unless specified in the SS-WP, for each analytical method, target compounds should include those listed in the Target Compound List (TCL) presented in NYSDEC ASP Appendix C. TCL for various analytical methods are presented in Table 6-A through Table 6-N.

Tentatively identified compounds (TICs) will be reported in the laboratory deliverables. If TICs or unknown compounds are detected at concentrations in excess of the applicable standards, criteria, and guidance (SCG), they should be addressed in either of two ways listed below. If a contaminant

specific SCG does not exist for TICs and for unknown compounds, the generic SCG (class of contaminant, e.g. SVOCs) should be used.

1. If the area will be remediated and it is likely that concentration of the TICs/unknown compounds will be reduced by the remediation, the TICs/unknown compounds should be analyzed in post remediation samples to document that they no longer exceed the applicable SCG.
2. An attempt should be made to positively identify and accurately quantify the TICs/unknown compounds using an analytical method consistent with this section so that a remediation standard can be developed.

7.5 TISSUE SAMPLING AND ANALYSIS

If tissue analysis is required, the following QA procedures should be followed.

1. Analysis of lipid content is required for all organochlorine compounds.

2. For GC, detector systems other than mass spectrometers are required for identification and quantification of some analyte groups depending on the extraction method used during preparation of the tissue for analysis. Proposed methods should be proposed and approved prior to analysis.

3. General USEPA quality control recommendations for tissue are contained in the NYSDEC DER-10, Appendix 2C. Alternate QC requirements may be specified depending on the specific analysis being done.

4. The QAPP for tissue analysis should follow the outline in the USEPA publication “Preparation Aids for the Development of Category I Quality Assurance Project Plans” (EPA/600/8-91/003).

5. Tissue sampling should follow the current procedures for biota collection, preparation, and analysis as directed by the DER.

7.6 TOXICITY TESTING

If toxicity testing is required, the quality assurance procedures contained in the latest approved USEPA or ASTM methods or any method approved by the DER should be followed.

7.7 AIR SAMPLING

If air sampling is required, the SOPs specified in the method approved by the USEPA or/and NYSDEC for the sampling should be followed. QA procedures should follow the guidelines or direction of the USEPA and NYSDOH and should be recorded in the SS-WP.

8.0 DATA MANAGEMENT AND EVALUATION

The data reduction, verification, validation, assessment, and reporting procedures described in this section will ensure that: (1) the data are reviewed and documented; (2) transcription and data reduction errors are minimized; (3) complete documentation is maintained; and (4) the reported results are accurate, or qualified if necessary. Laboratory data reduction and verification procedures are required to ensure that the data deliverable(s) meet the overall project objectives. Data reduction, whether performed by instrumentation or manually, shall follow methodologies specified in the laboratory SOPs or approved analytical methods. Project-specific variations of general procedures, statistical approach, or formulas must be identified and be detailed in the SS-WP. Any variances from established procedures must be requested and approved in advance. Automated procedures shall be verified as required by USEPA's guidance on Good Automated Laboratory Practices (GALP, USEPA 2185); all software shall be tested with a sample set of data to verify its correct operation via accurate capture, processing, manipulation, transfer, recording, and reporting of data. Data are reported in hardcopy data package(s) and as EDDs.

8.1 DATA REVIEW REQUIREMENTS FOR SCREENING DATA

Parsons will complete a 100 percent review of all screening data. The screening data methods are identified in Table 3 and the calibration and QC requirements are presented in Table 17. Calibration and QC requirements not within acceptable limits will be recorded.

Screening data deliverables shall be prepared for all field analyses. The screening data performed at field shall be reported on the screening data report forms (as attached in Appendix C). All field and QC sample results, calibrations, and calibration verifications should be recorded in a field logbook or the data report forms to ensure proper verification of sample results. Parsons QA officer will be responsible for the review of the entire screening data report package, including the associated field records. The results of this review shall (1) determine if the project objectives have been met, and (2) calculate the completeness of the screening data for the project. These results shall be included in the screening data deliverable.

8.2 DATA REVIEW LABORATORY REQUIREMENTS FOR DEFINITIVE DATA

Scientifically sound data of known and documented quality that meet project quality objectives are essential for use in the decision-making process. Data review is the process whereby data are examined and evaluated to varying levels of detail and specificity by a variety of personnel who have different responsibilities within the data management process. This section presents requirements for the laboratory to conduct review of definitive data.

8.2.1 Laboratory Data Reporting Requirements

The laboratory shall submit a data report to Parsons within 30 (or otherwise specified by the SS-WP) calendar days of receipt of samples. Data report should consist of one hard copy of NYSDEC Category B (or equivalent) standard data package and an EDD. The laboratory deliverables should be consistent with the NYSDEC ASP requirements, presented in Appendix B of the ASP. All data shall be reported using the ASP Category B (or equivalent) and all deliverables will be in the CLP or CLP equivalent Format. The chemistry data package must contain adequate information and be presented in a clear, legible, concise, and consecutively paginated manner. The data package will include a sample data summary package and a sample data package. Data packages should be delivered in accordance with the schedule communicated from the project manager. Raw data (including electronic media) of all field samples, QC samples, standards, and blanks should be archived and be available upon request for 5 years from the date of generation in accordance with the USEPA (2005a) requirement.

8.2.1.1 Sample Data Summary Package

A Sample Data Summary Package shall be delivered separately (i.e., separated by rubber bands, clips or other means) directly preceding the Sample Data Package. Sample data forms shall be arranged in increasing project sample number order, considering both letters and numbers. The Sample Data Summary Package consists of copies of specified items from the Sample Data Package. The Sample Data Summary Package shall contain all data for all samples within one SDG of the Case and shall be ordered as follows.

1. NYSDEC Data Package Summary Forms
2. SDG Narrative
3. By fraction (VOA, SV, PEST, INORG, CONV) and by sample within each fraction - tabulated target compound results (Form I-ORG or Form I-IN) and tentatively identified compounds (Form I-ORG, TIC) (VOA and BNA only)
4. By fraction (VOA, SV, and PEST) - surrogate spike analysis results (Form II-ORG) by matrix (water and/or soil) and for soil, by concentration (low or medium)
5. By fraction (VOA, SV, and PEST) - matrix spike/matrix spike duplicate/matrix spike blank results (Form III-ORG) - as required by method.
6. By fraction (VOA, SV, and PEST) - QC Check Sample/Standard Recovery Summary - If required by method.
7. By fraction (INORG and CONV only) - duplicate sample results (Form VIIN)
8. By fraction (INORG and CONV only) - spike sample results (Form V-IN)

9. By fraction (VOA, SV, PEST, INORG, CONV) - blank data (Form IV-ORG and Form III-IN) and tabulated results (Form I-ORG and Form I-IN) including tentatively identified compounds (Form I-ORG, TIC)(VOA and BNA only).
10. By fraction (VOA and SV only) - internal standard area data (Form VIIIORG).

8.2.1.2 Sample Data Package

The Sample Data Package is divided into the following eight major units, if applicable: SDG case narrative, Contract Lab Sample Information Sheets, COC forms, CLP volatiles data, CLP semivolatiles data, CLP pesticide/aroclor data, inorganic data. The CLP data for volatiles/semivolatiles/pesticide/aroclor data include QC summary, sample data, standards data, raw QC data, copy of calculations, and copy of extraction. The inorganic data portion includes inorganic sample results, QC data, verification of instrument parameters, raw data, copy of calculations, and digestion logs. The data package should be prepared consistent with the NYSDEC ASP and the forms specified in the NYSDEC ASP will be used for the data package. If the analysis of a fraction is not required, then that fraction-specific unit is not required as a deliverable.

The Sample Data Package shall include data for analyses of all samples in one SDG, including field samples, reanalyses, blanks, duplicates, LCSs, LCSDs, MSs, and MSDs.

The Laboratory shall retain a copy of the Sample Data Package for 365 days after final acceptance of data. After this time, the Laboratory may dispose of the package.

The Sample Data Package shall contain:

- Laboratory name and location (city and state);
- Project name and unique report ID number;
- Field sample ID number as written on custody form;
- Laboratory sample ID number;
- Matrix;
- Sample description;
- Sample preservation or condition at receipt;
- Date sample collected;
- Date sample received;
- Date sample extracted or prepared;
- Date sample analyzed;
- Method (and SOP) numbers for all preparation, cleanup, and analysis procedures employed;
- Preparation, analysis, and other batch numbers;
- Analyte or parameter;

- RLs adjusted for sample-specific factors (e.g., aliquot size, dilution or extraction factors, moisture content);
- Method detection limits;
- Analytical results;
- All confirmation data;
- Any data qualifiers assigned;
- Concentration units;
- All reported data will reflect any dilutions or concentrations. The dilution factor, if applicable, should be noted on the analytical report. If neat and/or diluted results are available, data from all runs should be recorded and reported;
- Percent moisture or percent solids (results of all soils, mulch, etc. are to be reported on a dry weight basis);
- Sample aliquot analyzed;
- Final extract volume;
- Case narrative describing all non-compliant issues;
- COC forms and sample receipt documentation;
- Verification of hold time compliance;
- Results for RL check standards for organic methods;
- Analytical batch control records including method blank results, LCS/LCSD and MS/MSD recoveries, and surrogate spike recoveries;
- Documentation that IS area counts and RTs meet criteria;
- Documentation that interference check samples met criteria for ICP and ICP-MS metals;
- Results for dilution test and post digestion spikes analyzed for metals;
- "Before" and "after" chromatographs of each manual integration (MI) event including the reason(s) for the MI, the signature of the analyst who performed the MI and the signature of the approver;
- Corrective action reports with problem, action, and results; and
- Completeness of the data.

8.2.1.3 Case Narrative Requirements

An important part of the laboratory documentation is the case narrative. The case narrative contains essential information that affords an informed evaluation of data usability. The case narrative shall be clearly labeled "SDG Narrative" and shall contain: laboratory name and location, case number; SDG number; sample numbers in the SDG, differentiating between initial analyses and re-analyses; contract number; project name and site location; and detailed documentation of any QC, sample, shipment, and/or analytical problems encountered in processing the samples reported in the data package.

Whenever data from sample re-analysis are submitted, the laboratory shall state in the SDG Narrative for each re-analysis, whether it considers the re-analysis to be billable, and if so, why.

The laboratory must also include any problems encountered: both technical and administrative, corrective actions taken, and resolution and an explanation for all data qualifiers (i.e. flags) applied to the data.

The SDG Narrative shall contain the following statement, verbatim: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on floppy diskette has been authorized by the Laboratory Manager or his designee, as verified by the following signature." This statement shall be directly followed by signature of the Laboratory Manager or his designee with a typed line below it containing the signer's name and title, and the date of signature.

The SDG Narrative itself must be signed in original signature by the Laboratory Manager or his designee and dated.

In summary, the following elements should be included in the case narrative:

- Cooler temperature, as required by the NYSDEC ASP.
- Table summarizing samples received, correlating field sample numbers, laboratory sample numbers, and laboratory tests completed.
- Discussion of sample appearance and integrity issues that may affect data usability (temperature, preservation, pH, sample container type or volume, air bubbles, multiphasic samples, excess headspace in soil VOC containers, the presence of multiple phases, etc.)
- Samples received but not analyzed and why.
- Discussion of holding time excursions for sample preparation and analyses.
- Analysis of all out-of-control or discrepancies of calibrations, continuing calibrations or QC sample results (surrogates, LCS, MS/MSD, post-digestion spikes, etc.), raw data/chromatograms and corrective actions taken.
- Identification of samples and analytes for which MI was necessary.
- Discussion of all qualified data and definition of qualifying flags.
- Discussion and recommendations of potential data usability of qualified data including detailed discussion of conditions associated with Q-flagged data.

8.2.1.4 Requirements for Reconstructed Total Ion Chromatograms

Reconstructed Ion Chromatograms (RIC) should be reported for each sample or sample extract. RICs must be normalized to the largest non-solvent component and contain the following header information:

- Sample number
- Date and time of analysis
- GC/MS instrument ID

IS and system monitoring compounds are to be labeled with the names of compounds, either directly out from the peak, or on a printout of RTs if RTs are printed over the peak. If automated system procedures are used for preliminary identification and/or quantification of the target compounds, the complete data system report must be included in all Sample Data Packages in addition to the RIC. The complete data system report shall include all of the information listed below. For laboratories that do not use the automated data system procedures, a laboratory "raw data sheet", which contains the following information, must be included in the Sample Data Package in addition to the chromatogram.

- Sample number
- Date and time of analysis
- RT or scan number of identified compounds
- Ion used for quantitation with measured area
- Copy of area table from data system
- GC/MS instrument ID
- Laboratory file ID

In all instances where the data system report has been edited, or where MI or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report.

8.2.1.5 Requirements for Reporting Compound Identification

For each sample, by each compound identified, the following shall be included in the data package:

a) copies of raw spectra and copies of background-subtracted mass spectra of target compounds listed in NYSDEC ASP that are identified in the sample and corresponding background-subtracted TCL standard mass spectra. Spectra must be labeled with NYSDEC sample number, lab file ID, date and time of analysis, and GC/MS instrument ID; compound names must be clearly marked on all spectra.

b) copies of mass spectra of organic compounds not listed in the TCL (TICs) with associated best-match spectra (three best matches).

8.2.1.6 Requirements for Reporting Compound Quantitation

The laboratory must provide a copy of the calculations work sheet showing how final results are obtained from values printed on the quantitation report. If manipulations are performed by a software package, a copy of the formula used must be supplied as well as values for all terms in the formula.

8.2.1.7 Reporting Limits Requirements

Reporting requirements associated with RLs are presented as follows:

- MDLs and sample results should be reported to one decimal place more than the corresponding RL, unless the appropriate number of significant figures for the measurement dictates otherwise.
- Soil samples shall have results reported on a dry weight basis. A wet weight aliquot of sample equivalent to the method specified dry weight aliquot of sample should be taken for analysis. Alternatively, the lab may choose to use a consistent wet weight aliquot that is expected to be large enough to compensate for the moisture in the sample (e.g., 50% more) and use this as a consistent weight.
- If possible, samples should be analyzed undiluted and non-detects reported to the project specified RLs. RLs for minority constituents in highly contaminated samples may have to be adjusted for dilutions.
- If the non-detect "ND", "U", "<", or other lower limit reporting convention is used, then these terms must be defined (EM200-1-6).
- RLs should be below the CRQL, if applicable.

8.2.1.8 Environmental Data Significant Digits Reporting Requirements

Definitive analytical data possess some degree of uncertainty in the final reported values. Use of scientifically defensible and consistent numbers of significant figures in reporting analytical data allows the readers and users of these data to properly evaluate measurement uncertainty. This proper evaluation of data accuracy and precision facilitates the scientifically valid interpretation, summarization and subsequent reporting of these data. The recommendations stated in this section of the SAP do not set policy for determining the number of significant figures laboratories should use in reporting their data. However, subcontractors and Parsons staff are encouraged to use sound scientific judgment in choosing the appropriate number of significant figures and to be consistent in the number of significant figures used to report definitive analytical data. The laboratories and Parsons project team are encouraged to comply with *Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications* (ASTM Designation: E 29-02, 2002).

8.2.2 Manual Integrations (MI)

MIs are an integral part of the chromatographic analysis process; they should be used judiciously to correct any incorrect integration by the automated instrumentation and not as a routine procedure for the purpose of meeting calibration or method QC acceptance criteria. Improper use of MIs (for example, peak shaving or peak enhancement) are considered improper, unethical, or illegal actions if performed solely to meet QC requirements. MIs shall be done only as a corrective action measures. Examples of instances where MI would be warranted include, but are not limited to, co-eluting compounds resulting in poor peak resolution, a misidentified peak, an incorrect RT, or a problematic baseline. When MIs are used, the following procedures are to be implemented for documenting the event and for consistency in performing the MI:

- The laboratory should provide SOP for MIs, if warranted. This SOP shall specify when automated integrations by the instrument are likely to be unreliable, what constitutes an unacceptable automated integration, and how the problems should be resolved by the analyst. This includes procedures for the analyst to follow in documenting any required MIs.

- When MIs are performed, raw data records shall include a complete audit trail for those manipulations. The raw data records shall include the results of both the automated and manual integrations (i.e., "before" and "after" chromatograms of manually integrated peaks), notation of the cause and justification for performing the MIs, and date, and signature/initials of person performing the manual operations.

- All MIs must be reviewed and approved by the laboratory Section supervisor and/or the laboratory QA officer.

  Note: Both the primary and secondary reviews (analyst's and supervisory) may be performed electronically, provided all documentation and data integrity are maintained.

- All MIs must be identified in the case narrative. This will ensure consistency when MIs are performed and facilitate review and acceptance of manually integrated data.

8.2.3 Tentatively Identified Compounds (TICs)

TICs are compounds not associated with the calibration standards, which are identified in methods with MS detection. All peaks with a response greater than 10% of the nearest IS are potential TICs and should be examined and reported. Qualitative identification of TICs is performed by computer searches of standard reference libraries and TICs may be reported as a specific chemical or as a member of a chemical family. For each volatile sample, the Laboratory shall conduct a search to determine the possible identity of up to 10 organic compounds of greatest concentration that are not

system monitoring compounds or ISs and are not listed as volatile TCL. For each semivolatile sample, the Laboratory shall conduct a search to determine the possible identification of up to 20 organic compounds of greatest concentration, which are not surrogates or ISs and are not listed as semivolatile TCL. In performing searches, the NIST/USEPA/NIH (2005 or later) and/or equivalent, mass spectral library shall be used. Concentrations are estimated assuming a RF of 1 between the TIC and the nearest IS.

8.2.4 Laboratory Data Review Requirements

All analytical data generated by the laboratory shall be verified prior to submittal to Parsons. This internal data review process, which is multi-tiered, shall include all aspects of data generation, reduction, and QC assessment. Procedures for laboratory verification and validation of data should be summarized in the laboratory QA manual. Each result reported by the laboratory should undergo multiple levels of internal data review. The analysts and technicians provide primary data review for 100 percent of the definitive data at the bench level, secondary review should be performed by independent experienced QC personnel on 100 percent of the data, and the final data packages are reviewed by the laboratory's section supervisor, QA manager, customer service representative or project contact before submission to Parsons.

The following elements for review/verification at each level must be included, but not be restricted to, in the review conducted by the laboratory:

- Sample receipt procedures and conditions,
- Sample preparation,
- Appropriate SOPs and analytical methodologies,
- Accuracy and completeness of analytical results,
- Correct interpretation of all raw data, including all MIs,
- Appropriate application of QC samples and compliance with established control limits.
- Verification of data transfers,
- Documentation completeness (e.g., all anomalies in the preparation and analysis have been identified, appropriate corrective actions taken, and have been documented in the case narrative(s), associated data have been appropriately qualified, anomaly forms are complete), and
- Accuracy and completeness of data deliverables (hard copy and electronic).

8.2.5 Laboratory Data Evaluation

The calibration, QC, and corrective actions for definitive data are shown in Tables 7-A through Table 12. Data qualifiers shall be applied by the laboratory as part of their validation activities. The data qualifiers for definitive data should be specified in the data deliverable package. Flagging criteria apply when acceptance criteria are not met and corrective actions were not successful or not

performed. The data qualifiers are reviewed by the supervisor of the respective analytical sections after the first and second level reviews of the laboratory data have been performed. No qualifiers will be applied to TICs.

The laboratory QA section shall perform a 100 percent review of 10 percent of the completed data packages, and the laboratory project representative shall complete a final review on all the completed data packages.

Parsons will subsequently evaluate the flags applied by the laboratory as part of the data validation and usability assessment activities. The flags may be accepted, modified, or rejected. For all data qualifiers that are changed, Parsons will provide clear justification for those modifications based on project-specific quality objectives.

8.2.6 Method Blank Evaluation Guidance

The following criteria shall be used to evaluate the acceptability of the blank data, unless PQOs specify otherwise. For method blanks, the source of contamination shall be investigated and measures shall be taken to correct, minimize, or eliminate the problem if the concentration exceeds the RL (Use the limits specified in Table 7-A through 7-G for common laboratory contaminants.). If the RL is exceeded, the laboratory shall evaluate whether reprocessing of the samples is necessary, based on the following criteria: i) the method blank contamination relative to the measured concentration of any sample in the associated preparation batch, or ii) there is evidence the blank contamination otherwise affects the sample results. Except when the sample analysis resulted in a non-detect, all samples associated with method blank contamination and meeting these criteria shall be reprocessed in a subsequent preparation batch. If no sample volume remains for reprocessing, the results shall be reported with appropriate flag, along with any other appropriate data qualifier. If an analyte is found only in the method blank, but not in any batch samples, no flagging is necessary. Method blanks should also be examined to verify that any TICs present in the samples are not found in the blank. Method blank contamination must be addressed in the case narrative.

8.2.7 Laboratory Data Reduction

Data reduction is the process by which raw analytical data generated from laboratory instrument systems are converted into usable concentrations. The raw data, which may take the form of area counts, instrument responses or observations, are processed by the laboratory and converted into concentrations expressed in the parts-per-million (ppm) or parts-per-billion (ppb) range. Raw data from these systems include compound identifications, concentrations, RTs, and data system printouts. Raw data are usually reported in graphic form, bargraph form, or tabular form. The laboratories will follow the applicable data reduction SOPs for data reduction requirements. Concentration units are to be listed on reports and any special conditions, such as dry weight conversions will be noted. “Non-

detects" will be reported as less than the practical quantitation limit (PQL). Results reported greater than the MDL but less than the PQL will be reported as estimated and flagged by the laboratory.

8.3 DATA TRANSFORMATION AND DATA REDUCTION

Field personnel will record all field data in bound field notebooks and on standard forms. During processing of field data, validation checks will be performed by individuals designated by the project manager. The purpose of these checks is to identify "outliers;" that is, data which do not conform to the pattern established by other observations. Because of the limited number of observations, detailed statistical analysis of the data to be obtained during this project is not feasible, and the principal method of validation will be routine checks to assure that data are correctly transcribed and that reported identification codes and sampling information match the corresponding information in the field records. In addition, data will be compared against those obtained in previous investigations (where available) and against applicable standards and guidelines.

Although outliers may be the result of transcription errors or instrumental breakdowns, they may also be manifestations of a greater degree of spatial or temporal variability than expected. Therefore, after an outlier has been identified, a decision must be made concerning its further use. Obvious mistakes in data will be corrected when possible, and the correct value will be inserted. If the correct value cannot be obtained, the data may be excluded. An attempt will be made to explain the existence of the outlier. If no plausible explanation can be found for the outlier, it may be excluded, but a note to that effect will be included in the report. Also, an attempt will be made to determine the effect of the outlier when both included and excluded in the data set, and the results will be discussed in the report.

After checking the validity of the data in the field notes, the field team leader or his designee will reduce the data to tabular form, when possible, by entering the data into data files. Where appropriate, the data files will be set up for direct input into the project database. At a minimum, 10% of the data entered into the database will be verified through a QC process. Subjective data will be filed as hard copies for later review by the project manager and incorporation into technical reports, as appropriate.

Sample calculations are contained in the method specifications. All concentration data shall be expressed in units of micrograms per liter (ug/L) or micrograms per kilogram (ug/Kg) dry weight, as appropriate for the matrix. The field measurements of pH, conductivity, turbidity, and temperature shall be reported in standard logarithmic, umho/cm, nephelometric turbidity units (NTUs), and degrees Celsius, respectively. All definitive analytical values and screening measurement values should be reported to appropriate significant figures consistent with the measurement. As an example, all water levels measured in wells will be reported to the nearest 0.01 foot and soil sampling depths will be reported to the nearest 0.1 foot.

All analytical results are carefully reviewed and formatted into final submittal form by experienced QC personnel. The data will be input into the project database, as described in Section 8.11.2.

8.4 DATA ASSESSMENT PROCEDURES

Scientifically sound data of known and documented quality that meet PQOs are essential for use in the decision-making process. Data assessment is the process whereby data are examined and evaluated to varying levels of detail and specificity by a variety of personnel who have different responsibilities within the data management process. For definitive data, the data assessment includes data verification, validation, and usability assessment. For screening data, data verification will be conducted to ensure data quality. There must be persuasive records that document data review activities to afford effective assessment of the data for its quality and usability. The data can then move forward with associated qualifiers indicating the overall usability of the data.

Data verification is the first step in data review. As used here, data verification is confirmation that the specified requirements have been performed, i.e., it is a completeness check. The detailed discussion of data verification is presented in Section 8.5.

Data validation extends this and is confirmation that the requirements for a specific intended use are fulfilled. Data validation is the systematic process of evaluating the compliance of the data with the pre-defined requirements of the project, including method, procedural, or contractual requirements and the comparison of the data with criteria based on the quality objectives documented in this SAP and the SS-WP. The purpose of data validation is to assess the performance associated with the analysis in order to determine the quality of the data. Data validation includes a determination, to the extent possible, of the reasons for any failure to meet performance requirements, and an evaluation of the impact of such failures on the usability of the data. Data validation procedure is presented in Section 8.6.

The data usability assessment is an evaluation based on the results of data validation and verification in the context of the overall project decisions or objectives. The assessment determines whether the project execution and resulting data meet PQOs. Both the sampling and analytical activities must be considered, with the ultimate goal of assessing whether the final, qualified results support the decisions to be made with the data. The requirements for data usability assessment are presented in Section 8.7.

8.5 DATA VERIFICATION

Data verification is the most basic assessment of data. Data verification is a process for evaluating the completeness, correctness, consistency, and compliance of a data package against a standard or contract. In this context, "completeness" means all required hardcopy and electronic deliverables are

present. Data verification will be performed by Parsons for all laboratory delivered data and field screening data.

8.6 ANALYTICAL DATA VALIDATION

Based on the information in the data package, a reviewer should be able to determine the precision, accuracy, representativeness, completeness, comparability, sensitivity, and defensibility of the data.

Data validation for laboratory data will be performed for all definitive sample results in accordance with the requirements contained in the analytical method, the SAP andSS-WP, the NYSDEC ASP, the USEPA Region 2 SOPs, the USEPA National Functional Guidelines for Data Review (USEPA, 2005b, 2004a). 100% data validation will be manually performed by the project chemist or personnel trained by the project chemist. The project chemist will review at least 20% of the data validated by the trained personnel and is responsible to oversee the whole data validation process. In performing the data validation, the raw data are spot-checked in accordance with the Region 2 SOP to evaluate whether there is any transcription error. The review of laboratory data will focus on the following subjects, if applicable:

- COC forms,
- Holding times, sample preservation, and sample conditions (e.g., percentage of solids),
- Instrument calibration and performance,
- Method blanks, trip blanks, equipment/rinsate blanks,
- MDLs and laboratory-established RLs,
- Analytical batch control records including laboratory spike recoveries and spike duplicate results, and MS recoveries and MSD results,
- Surrogate standard recoveries,
- IS areas and RTs,
- Confirmation results for explosives,
- Chromatograms and mass spectrums,
- Corrective actions,
- Formulas used for analyte quantitation,
- Laboratory and field duplicate results,
- Calculations supporting analyte quantitation,
- ICP serial dilution,
- ICS results,
- ICP linear range, and
- Completeness of data.

Data outliers that fall outside of the QC criteria outlined in this SAP or SS-WP (e.g., Tables 5-A/B, Table 7-A through Table 7-G, Table 8, and Table 9-A through Table 9-G, Table 10-A through 10-E, and Table 12) will be flagged with an appropriate qualifier consistent with the USEPA Region 2 SOPs. All data validation flags applied will be added to the validated data with explanation prior to submittal. Data validation flags are provided in Table 18-A and Table 18-B for inorganics and organics, respectively. An example form that will be used for the data validation is provided in Tables 19-A, 19-B, and 19-C. Table 20 summarizes data validation criteria for QA/QC parameters and corresponding data qualification action.

8.7 DATA USABILITY ASSESSMENT

A usability assessment evaluates whether data meet PQOs as they relate to the decision to be made, and evaluates whether data are suitable for making that decision. All types of definitive data (e.g., sampling, on-site analytical, off-site laboratory) are relevant to the usability assessment. The usability assessment is the final step of data review and can be performed only on data of known and documented quality (i.e., verified and validated data).

A data usability assessment report will be submitted to the project manager by the Parsons project chemist to summarize the usability of the validated data. The report will include:

- A summary of data validation results,
- Overall data usability and completeness,
- Evaluation of each data quality indicator (whether meet the criteria, what potential impacts on data usability),
- Any deviations (e.g., holding time, QC performance criteria, sample location, sample collection SOPs) from the SAP and/or the SS-WP and the impact of deviations on the usability of data,
- Any problems with documentation or custody procedures and the impact on the usability of data,
- Damaged samples and the usability of the associated data, and
- Any other relevant issues.

8.8 NON-DIRECT MEASUREMENT DATA EVALUATION

Site-specific non-direct measurement data evaluation will be specified in the SS-WP. Non-direct measurement data that will be collected for the project include

- Site data from all previous investigations, and
- measurements that are ancillary to addressing the project's objectives (e.g., meteorological data)

Existing data will be evaluated in combination with newly collected data. An evaluation consistent with the USEPA QA/G-5 (2002a) and USEPA (2005a) Uniform Federal Policy for Quality Assurance Project Plans will be conducted to assess whether existing data meet the current project's acceptance criteria before the existing data are used for decision-making and will be recorded in project-specific work plan.

8.9 RECONCILIATION WITH USER REQUIREMENTS

Project results will be reconciled with the requirements defined by the data user or decision maker. Based on site-specific DQOs, the approach of data reconciliation will be discussed in SS-WP or SAP. Limitations on the use of the data will be reported in the project technical report.

8.10 ELECTRONIC DATA REPORTS

The laboratory shall provide an EDD in the format as specified in the NYSDEC ASP (Exhibit H) and in this generic SAP. Minimum specifications and requirements for EDDs are attached in Appendix D.

The laboratories will submit both a hard copy and an electronic copy of the analytical data for environmental, field and laboratory QC samples. The EDD shall contain the same information as described for the hard copy deliverable. Electronic deliverables should be reported with no discrepancies from the hard copy. In general, the EDD submittal will include:

- the laboratory's ID of each field sample,
- field sample IDs,
- analytes,
- results,
- data qualifiers and validation flags,
- concentration units, and
- applicable QC data.

Additionally, the calibration information should be included in the EDD if the laboratory has that capability.

The project technical data other than the chemical analysis results such as site information; well characteristics; hydrogeologic, geologic, and physical analysis results will be recorded by Parsons as electronic files under the project directory.

8.11 PROJECT DATA TRACKING AND ARCHIVING

This section presents information on project data tracking (Section 8.11.1), archiving (Section 8.11.2), storage and retrieval (Section 8.11.3), and submittal (Section 8.11.4).

8.11.1 Data Tracking

Project manager will be responsible for tracking data as they are collected, transformed or reduced, transmitted, analyzed, and submitted. Reports produced during each of the above phase will be submitted to project manager and archived in project files to ensure the data are properly tracked, reviewed, and validated for use.

8.11.2 Data Archiving

This section presents archiving procedures for electronic data (Section 8.11.2.1) and hardcopy data (Section 8.11.2.2).

8.11.2.1 Electronic Data Archiving

Electronic data shall be archived in project files and in electronic format by Parsons and the laboratory for the duration of the project or a minimum of five years, whichever is longer, or as dictated by project requirements (if longer than five years). The laboratory shall also provide for Parsons and Huntsville all files associated with the project in electronic media. The data packages must be retrievable for Parsons and Huntsville within seven calendar days. In the event of laboratory closure, all applicable documents and electronic media must be immediately transferred to Parsons or Huntsville.

The laboratory shall maintain electronic records sufficient to recreate each analytical event conducted pursuant to the SOW. The minimum records the laboratory shall keep contain the following: (1) COC forms, (2) initial and continuing calibration records including standards preparation traceable to the original material and lot number, (3) instrument tuning records (as applicable), (3) method blank results, (4) IS results, (5) surrogate spiking records and results (as applicable), (6) spike and spike duplicate records and results, (7) laboratory records, (8) raw data, including instrument printouts, bench work sheets, and/or chromatograms with compound identification and quantitation reports, (9) corrective action reports, (10) other method and project required QC samples and results, and (11) laboratory specific written SOPs for each analytical method and QA/QC function in place at the time of analysis of project samples.

Parsons uses Windows (2000 or more recent version) system to perform electronic file operation and Oracle database or other appropriate programs to perform chemical analysis data management on

network computers. The software programs are commonly used and upgraded whenever software changes occur. Parsons performs scheduled electronic data backups of project files and performs periodic archiving of electronic media on a scheduled basis. Electronic project files are maintained on a no-fault server; a no-fault server minimizes data loss during hard-drive failure by operating and distributing data sequentially over four separate physical hard drives. Back-ups of project files on to magnetic tapes on the no-fault server are performed on a weekly basis and updated daily, Monday through Thursday, through a differential back-up. A differential back-up replaces backed-up files that are edited between each daily update differential back-up.

Electronic tape back-ups are stored in a fire proof box either at Parsons or at an off-site storage location. Weekly backups onto magnetic tape are retained for a minimum of three weeks prior to overwriting; however, the last back-up each month is retained without being overwritten.

8.11.2.2 Hard Copy Data Archiving

Hardcopy data shall be archived in project files by Parsons and the laboratory for the duration of the project or a minimum of five years, whichever is longer, or as dictated by project requirements (if longer than five years). The laboratory shall maintain hardcopy records sufficient to recreate each analytical event conducted pursuant to the SOW.

All field measurements and instrument check data will be entered into an electronic database where it will also be maintained. In addition, hardcopy of field measurements and field notes will be archived in project files by Parsons for the duration of the project or a minimum of five years, whichever is longer, or as dictated by project requirements (if longer than five years).

8.11.3 Data Storage and Retrieval

All hardcopy and electronic chemical analysis data, field sheets, log books, and other relevant field documents (e.g., health and safety meeting sign-in sheets, personnel daily frisking forms, daily instrument check sheets) will be maintained by Parsons at Parsons or at an off-site storage location. If stored, the data packages will be retrievable within seven calendar days.

8.11.4 Laboratory Data Submittal

After analytical results from laboratories are validated, the validated results will be submitted to the Army on a quarterly basis. If laboratory analytical results are decided not be validated based on the project needs, the original laboratory results will be submitted on a quarterly basis. Both hardcopy and electronic deliverables will be submitted. The Army will submit an electronic data copy to USEPA Region 2.

8.12 HARDCOPY DATA REPORT FORMS

The hardcopy data reports or forms shall conform to the formats identified in the NYSDEC ASP program. The NYSDEC ASP forms shall be used unless a variance is requested and approved in advance and that the forms included in the site specific work plan or SAP, can be verified that they contain at a minimum the information requested on the NYSDEC ASP forms. A complete list and description of forms is provided in the NYSDEC ASP. Other forms shall be included in the site-specific work plan, as needed.

For all analyses, at a minimum, the laboratory report will show traceability to the sample analyzed and will contain the elements presented below.

- Case narrative (identifies problems and corrective actions);
- Copy of signed COC;
- Cooler receipt forms documenting the date, time of receipt, condition of samples (including preservation) and labels, temperature of the shipping container, and verification of integrity of the custody seals;
- Laboratory name;
- Client name;
- Date of sample collection;
- Date of sample receipt;
- Date of sample extraction or preparation;
- Date of issue;
- Project name and unique identification number;
- Field sample name/number;
- Laboratory sample number;
- Sample matrix description;
- Analytical method description and reference citation for all analyses, preparation, cleanup procedures;
- Preparation, analysis and other batch numbers;
- Individual parameter;
- Analytical results with correct number of significant figures;
- All confirmation data, when performed;
- Date of analysis (first run and subsequent runs);
- Analysis time;
- Method reporting limits adjusted for sample-specific factors (i.e., aliquot size, dilution/concentration factors, moisture content;
- Method detection limits;

- Concentration units;
- Any data qualifiers assigned;
- Percent moisture or percent solids (all soils reported on dry weight basis);
- Any special conditions;
- Chromatograms, as needed;
- Sample aliquot analyzed;
- Final extract volume;
- Dilution or concentration factors (if dilutions result in non-detect values for all other analytes which showed detected concentrations in previous analyses, the results of both runs will be reported with the appropriate notations in the narrative);

- Initial and continuing calibration results;

- A cross-reference to identify applicable laboratory QC samples with field samples; and
- Corresponding QC summary report.

The laboratory reports should conform to the requirements presented in Section 8.2.1. QC data will be recorded on Contract Laboratory Program or CLP-equivalent QC summary forms for the appropriate tests and correlated to the analysis results by the laboratory lot control numbers. The QC results are used to prepare control charts for each test and matrix type. QC reports will contain the following items as appropriate:

- Narratives describing any non-compliant samples,
- Method blank, trip blank, equipment rinsate blank,
- Surrogate results,
- LCS/LCSD results,
- MS/MSD or MS/MD results, and
- Tuning results.

The laboratory will, as a part of the data reduction and validation process, confirm that its documentation is complete, sequentially paginated, and legible; qualitative identifications are accurate; calculations are accurate; and results are expressed in the appropriate units. The laboratory will also confirm that data documentation has been approved by the laboratory manager or designee.

Manual recording should be conducted legibly in ink, initialed and dated by the responsible person. Any changes in entries in laboratory notebooks or on computer-printed data shall be corrected by drawing a single line through the error, initialing, and dating the new entry. The use of correction tape or fluid is not acceptable. All changes made in the computer shall be traceable.

8.13 DATA ANALYSIS

Parsons uses windows (2000 or more recent version) system to perform general file/data processing and the Oracle database to perform chemical analysis data management on network computers. In addition, various software and/or computer codes will be used at different project stages for different data analysis purposes. The following lists some of the commonly used software/computer codes for the project:

- XLSTAT (version 6.1.9 by Addinsoft), used for background comparison or any other statistical comparison;

- The computer code AQTESOLV™ (Geraghty & Miller, 1994) or similar, and the method of Cooper *et al*. (1967) for confined aquifers or the method of Bouwer and Rice (1976) and Bouwer (1989) for unconfined conditions, slug testing data analysis;

- The USEPA (2004c) Software for Calculating Upper Confidence Limits (ProUCL version 3.00.02), risk assessment Exposure Point Concentration estimation;

- The Integrated Exposure Uptake Biokinetic Model for Lead in Children (IEUBK) developed by USEPA, risk assessment for child lead exposure;

- The Recommendations of the Technical Review Workgroup for Lead for an Interim Approach to Assessing Risks Associated with Adult Exposures to Lead in Soil (USEPA, 2003), risk assessment for adult industrial worker.

Software/computer codes used for project will be recorded in project technical document and project manager and technical personnel are responsible for identifying the appropriate software for the project and for using the most recent version of the software.

Detailed discussion of system backup can be found in Section 8.11.

9.0 PERFORMANCE ASSESSMENT AND SYSTEM AUDITS

Audits will include a careful evaluation of both field and laboratory quality control procedures. Audits of field procedures will be performed before or shortly after systems are operational. The audits will be conducted by an individual who is technically knowledgeable about the operation(s) under review. This section discusses procedures for both performance audits (Section 9.1) and system audits (Section 9.2).

9.1 PERFORMANCE AUDIT PROCEDURES

Performance audits are conducted by introducing control samples into the data production process. These control samples may include performance evaluation samples, field samples spiked with known amounts of analyte, and split field samples that are analyzed by two or more analysts within or without the organization.

9.1.1 Laboratory Performance Audits

In addition to conducting internal reviews and audits, as part of its established Quality Assurance program, the laboratory is required to take part in regularly scheduled Performance Evaluations and laboratory audits from State and Federal agencies. These are conducted as part of certification processes and to monitor the laboratory performance. The laboratory shall use the information provided from these audits to monitor and assess the quality of its performance. Problems detected in these audits shall be reviewed by the laboratory Quality Assurance Manager and laboratory management and corrective action shall be instituted as necessary.

The laboratory will be required to conduct an analysis of Performance Evaluation (PE) samples or provide proof that Performance Evaluation samples submitted by USEPA or a state agency have been analyzed within the past twelve (12) months.

9.1.2 Field Performance Audits

Unless specified by the site-specific work plan, field performance audits will not be conducted for this project. Field performance will be assessed using QA/AC results (e.g., trip blank, equipment/rinsate blank, field replicate analyses, sample condition upon receipt by the laboratory). Each blank analysis will be considered an indirect audit of the effectiveness of measures taken in the field to ensure sample integrity (e.g., field decontamination procedures). The results of the field replicate analyses are an indirect audit of the ability of each field team to collect representative sample portions of each matrix type. In addition, Parsons QA Officer will be responsible to review in detail field procedures and field logs to verify compliance.

9.2 SYSTEM AUDIT PROCEDURES

Systems audits are qualitative inspections and reviews of the quality assurance system used by some part of or the entire measurement system. The audits are performed against a set of requirements, which may be a quality assurance project plan or work plan, a standard method, or a project statement of work. The primary objective of the systems audits is to ensure that the QA/QC procedures are being followed.

Field and laboratory quality control procedures and associated documentation may be system audited. These audits will be performed once during the performance of the project. However, if conditions adverse to quality are detected or if the project manager requests, additional audits may occur.

System audits will also be performed by data users including USEPA Region 2, NYSDEC, and the Army. Generally, the audit covers the SAP development and approval and SOP development and approval.

9.2.1 Laboratory Systems Audits

As part of its Quality Assurance Program, the Laboratory Quality Assurance Manager shall conduct periodic checks and audits of the analytical systems. The purpose of these is to ensure that the analytical systems are working properly and that personnel are adhering to established procedures and documenting the required information. These checks and audits will also assist in determining or detecting where problems are occurring.

The laboratory Quality Assurance Manager will periodically review laboratory control samples. These samples will reflect the quality of the entire analytical method, the efficiency of the preparation method and the analytical instrument performance. When a problem is detected, the Quality Assurance Manager will assist the analyst and laboratory management in determining the reason and in developing a solution. Rechecking of systems will be conducted by the Quality Assurance Manager as required.

Parsons QA officer or his/her designee is responsible for reviewing the laboratory QA/QC manual and ensure the laboratory QA/QC procedures are consistent with the project SAP requirement.

9.2.2 Field System Audit Procedures

System audits of field activities will be accomplished by an inspection of all field site activities. Field system audit should be conducted at the beginning of any long-term field sampling program (i.e., >1 week) and will be conducted on an ongoing basis during the project as field data are generated, reduced, and analyzed. Field audits, if warranted, should be specified in the SS-WP.

During the field audit, the auditor(s) will compare current field practices with standard procedures. The following elements will be evaluated during a field system audit:

- All activities including sample collection, equipment calibration, decontamination, record keeping conducted in accordance with the generic SAP and/or site-specific work plan;
- All procedures and analyses conducted according to procedures outlined in the generic SAP and/or site-specific work plan;
- Sample documentation;
- Working order of instruments and equipment;
- Level of QA conducted per each field team;
- Contingency plans in case of equipment failure or other event preventing the planned activity from proceeding;
- Decontamination procedures;
- Level of efficiency with which each team conducts planned activities at one site and proceeds to the next; and
- Sample packaging and shipment.

All numerical manipulations, including manual calculations, will be documented. All records of numerical analyses will be legible, of reproduction-quality, and sufficiently complete to permit logical reconstruction by a qualified individual other than the originator. After completion of the audit, any deficiencies will be discussed with the field staff and corrections implemented. If any of these deficiencies could affect the integrity of the samples being collected, the auditor(s) will inform the field staff immediately, so that corrections will be implemented immediately. The audit will be performed by the project QA officer, project chemist, field team leader, or designees. A standard form of field audit report and field daily quality control report is provided in Appendix C.

Field system audit may also be conducted by regulators.

9.3 AUDIT REPORTS

Audit reports will be written by auditors who have performed the audit after gathering and evaluating all data. Items, activities, and documents determined by lead auditors to be in noncompliance shall be identified at exit interviews conducted with the involved management. Noncompliances will be logged and documented through audit findings, which are attached to and are a part of the integral audit report. These audit-finding forms are directed to Parsons project manager, the Army, and the regulators (contact information see Section 3) within fifteen days after the completion of the audit.

Serious deficiencies will be reported to the project manager within 24 hours to satisfactorily resolve the noncompliance in a specified and timely manner. All audit checklists, audit reports, audit findings, and acceptable resolutions are approved by the QAO prior to issue. Corrective actions should be followed if any noncompliance is noted in the audit report. Verification of acceptable resolutions may be determined by re-audit or documented surveillance of the item or activity. Upon verification acceptance, the QAO will close out the audit report and findings.

10.0 PREVENTATIVE MAINTENANCE

A preventative maintenance program is necessary to help prevent delays in project schedules, poor output performance or erroneous results in investigative operations. Preventative maintenance on laboratory analytical equipment used in this project will be performed contractually by qualified personnel. Maintenance of field equipment will be performed routinely for sampling events. More extensive maintenance will be performed based on hours of use, by a qualified servicing organization. Repairs, adjustments and calibrations will be recorded.

10.1 FIELD EQUIPMENT

The three elements of the field equipment maintenance program include normal upkeep of equipment, service and repair (when required), and formalized record-keeping of all work performed on each piece of equipment. This section addresses the normal equipment upkeep element of the maintenance program. For most of the equipment, normal maintenance will consist of cleaning outside surfaces, lubrication of all moving parts, and, if applicable, a battery level check and recharge or replacement as necessary. This program will include the maintenance of all monitoring, measuring, and test equipment returning from use or any equipment used on a daily basis. The frequency of maintenance checks will be dependent on the individual needs and use of each piece of equipment. Maintenance procedures will be only those necessary for keeping an instrument in service or in preparation for everyday use. It is beyond the scope of this document to cover repair procedures for each piece of equipment. Repair problems will be referred to the manufacturer or other qualified servicing organization.

The field team leader, or the designated personnel, will be responsible for keeping all maintenance records, making sure all equipment used is maintained properly, informing field team members of any specific maintenance requirements for equipment used at the site and shipping any instrument in need of repair to the correct source.

The field personnel responsibilities include maintaining each piece of equipment located at the site and the maintenance of equipment after use. A record of equipment maintenance and repair will be kept in the field logbook.

Table 11 summarizes requirement for field equipment calibration, maintenance, testing, and inspection. These requirements are also briefed discussed in the following sections.

10.1.1 Field Equipment Calibration

The frequency of calibration for field instruments will be performed at the intervals specified by the manufacturer or more frequently as conditions dictate, but daily as a minimum. To ensure comparability between sample data of similar samples and sample conditions, standard solutions and material traceable to the National Institute of Standards and Technology or USEPA-published standards/protocols will be used to calibrate the field instruments. Table 11 summarizes requirement for field equipment calibration.

10.1.2 Field Equipment Inspection

Equipment to be used during field sampling will be examined to certify that it is in proper operating condition. This includes checking the manufacturer's operating manual and the instructions for each equipment to ensure that all maintenance requirements are being observed. Field notes for previous sampling trips will be reviewed so that the notations on any prior equipment problem are not overlooked and all necessary repairs to equipment have been carried out.

10.1.3 Field Equipment Maintenance

Equipment, instruments, tools, gauges, and other items requiring preventive maintenance will be serviced in accordance with the manufacturer's specified recommendations and written procedures developed by the operators.

Manufacturer's procedures identify the schedule for servicing critical items in order to minimize the downtime of the measurement system. It will be the responsibility of the field team leader to adhere to the maintenance schedule and to arrange any necessary and prompt service as required. Service to the equipment, instruments, tools, gauges, etc., will be performed by qualified personnel. In the absence of any manufacturer's recommended maintenance criteria, a maintenance procedure will be developed by the operator based upon experience and previous use of the equipment.

Logs will be established to record maintenance and service procedures and schedules. All maintenance records will be documented and traceable to the specific equipment, instruments, tools, and gauges.

Critical spare parts for field equipment will be located in the Parsons office at the Seneca Depot (Building 125). Records documenting field equipment calibration, maintenance, testing, and inspection activities will be archived under project file.

10.2 RENTAL EQUIPMENT

Rental equipment used on the project should be obtained only from a certified rental supplier. The equipment will require a prereceipt to verify accuracy, maintenance and upkeep of the equipment. A receipt indicating that the equipment has been checked upon return will be required as well.

10.3 LABORATORY INSTRUMENT

An important factor in maintaining accuracy and precision, achieving required holding times, and addressing contract schedule is preventive laboratory instrument maintenance. As part of the laboratory's maintenance program, service contracts are held on critical analytical instruments. SOP's for routine maintenance of laboratory equipment shall be submitted to Parsons by each laboratory performing analytical services.

10.3.1 Laboratory Instrument Calibration

All laboratory instruments shall be calibrated in accordance with USEPA SW-846 analytical methodology and the requirements of the NYSDEC ASP.

10.3.2 Laboratory Instrument Maintenance

An important factor in maintaining accuracy and precision, achieving required holding times, and addressing contract schedule is preventive maintenance. As part of the laboratory's maintenance program, service contracts are held on critical analytical instruments. SOP's for routine maintenance of laboratory equipment are included as part of the laboratory QA manual and will be reviewed by project chemist before project starts. The SOPs submitted by the laboratory describe the procedures and documentation activities that will be performed to ensure that all analytical instrumentation and equipment are available and in working order when needed. The SOPs also discuss the ability to ensure that project schedules are met (e.g., availability of spare parts or spare instruments, instrument control (on-site and during storage), security, and availability (e.g., log-in/log-out procedures)).

Instrument and equipment maintenance logs must be kept to document analytical instrumentation and equipment maintenance, testing, and inspection activities.

11.0 NONCONFORMANCE/CORRECTIVE ACTIONS

A nonconformance is defined as an identified or suspected deficiency in an approved document, such as a technical report, calculation, or computer program; an item where the quality of the end item itself or subsequent activities using the document or item would be affected by the deficiency; or an activity that is not conducted in accordance with the established plans or procedures. When a significant condition adverse to quality is noted at the site or laboratories by the field staff and/or Project Chemist, the cause of the condition will be determined and corrective action taken to preclude possible repetition. Condition identification, cause, reference documents, and corrective action planned will be documented and reported to the Parsons project manager, Parsons QA officer, the USACE Project Chemist, and involved subcontractor management. Implementation of corrective actions will be verified by documented follow-up action. All project personnel have the daily responsibility to promptly identify and report any condition adverse to quality, as well as to solicit the approved corrective action.

Parsons project manager has overall responsibility to ensure that all corrective actions necessary to resolve audit findings are acted upon promptly and satisfactorily. The project manager shall ensure that no further work dependent on the nonconforming item or activity is performed until the nonconformance is corrected. Samples that are analyzed prior to the resolution of a nonconforming event will be re-sampled, and/or reanalyzed once the corrective action has been initiated and is proven effective.

A copy of each closed nonconformance report shall be included in the quality assurance file and shall be maintained by the Project QA Officer. A template of nonconformance and corrective action report is provided in Appendix C.

11.1 FIELD CORRECTIVE ACTION

A corrective action shall be initiated during the field work when precision, accuracy, completeness, representativeness or comparability are not met or changes are made in the field that do not meet the scope of work requirements or other conditions are identified that are not consistent with the SAP. To document, a report shall be filed which lists the problems encountered and the corrective action implemented. A stop-work order may be issued by the Project QA Officer, if no resolution can be reached.

11.2 LABORATORY CORRECTIVE ACTION

If QA results for a particular analysis are outside the performance criteria described in this SAP or site-specific work plan (e.g., performance criteria for DQIs presented in Section 4) corrective action

will be taken to ensure continued data quality. Corrective actions that may be taken include, but are not limited to:

- Rechecking calculations;
- Checking QC data on other samples;
- Auditing laboratory procedures;
- Repreparing and/or reanalyzing the sample if warranted;
- Accepting data with the acknowledged level of uncertainty; and
- Qualifying the data as unusable.

The laboratory QA Manager will be responsible for initiating laboratory corrective action within 48 hours of the time it was noted.

12.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

QA reports will be generated by Parsons and corresponding laboratories during the project. In addition, audit and performance evaluation reports will be submitted by auditors to management to ensure the quality of the project.

12.1 LABORATORY QA REPORTS

The laboratory will summarize pertinent QA/QC issues in the laboratory data package case narrative report. These reports will include discussions of any conditions adverse or potentially adverse to quality, such as:

- Any laboratory or sample conditions which necessitate a departure from the methods or procedures specified in this plan,
- Any missed holding times or problems with laboratory QC acceptance criteria, and
- The associated corrective actions undertaken.

Such reports shall not prevent early notification to project management of such problems when timely notice can reduce the loss or potential loss of quality, time, effort, or expense.

12.2 FIELD QA REPORTS

Any field-related QA memorandums or forms shall be forwarded by field team leaders to the project manager, who will ensure that the project QA officer receives copies. The project technical director and project manager (or designated individual) will review these reports for completeness and the appropriateness of any corrective actions. The reports will be retained in the project files, and will be summarized in the QA report included in the final project documents. Appropriate steps will be taken to correct any QA/QC concerns as they are identified. The Parsons project manager will ensure that the technical project manager is informed of any significant QA/QC developments.

12.3 REPORTS OF AUDIT AND PERFORMANCE EVALUATION

As discussed in Section 9.3, audit reports will be written by auditors who have performed the audit within fifteen days after the completion of the audit. Serious deficiencies will be reported to the project manager within 24 hours to satisfactorily resolve the noncompliance in a specified and timely manner. The audit reports are directed to Parsons project manager, the Army, and the regulators (contact information see Section 3).

12.4 PROJECT QA REPORTS

A project QA report will be submitted after the project sampling and analysis is completed as part of the technical report. The QA report will summarize the overall QA information of the project, including information of laboratory performance, field performance, system performance, audit findings, and corrective actions. In addition, both validated data and laboratory and field QC data will be presented. The laboratory QA reports, field QA reports, project audit reports, and corrective action reports will be used to assist in developing the final QA Report. The project QA report does not prevent internal QA memorandums or communications regarding QA issues.

The following elements, if applicable, will be addressed in the QA section or other section of the technical report:

- Project scope,
- Project description,
- Status of project,
- Sampling procedures (planned vs. implemented),
- Field quality control activities (planned vs. implemented),
- Analytical procedures,
- A summary of data usability assessments in terms of precision, accuracy, representativeness, completeness, comparability, and sensitivity,
- Any problems that could affect the quality of the data collected, the project schedule or the completion of the project,
- Changes in the project's experimental design, objectives, or staffing,
- The need for additional equipment to achieve project objectives, or any problems with equipment,
- Data presentation,
- Required corrective actions and effectiveness of corrective action implementation,
- Limitations on the use of measurement data generated, and
- Lessons learned

13.0 SAP REVISIONS AND DISTRIBUTION

This section presents procedures and requirements for SAP revisions (Section 13.1) and distribution (Section 13.2).

13.1 SAP REVISIONS

The generic SAP will be revised and updated every five years in accordance with USEPA (2005a) requirement, or when there are changes warranted in response to project needs, or when directed by the approval authority. The project manager, QAO, and project chemist are responsible to determine if any changes to the SAP are warranted and their impacts to the quality of the project. If a change is desirable, the change will be incorporated into the site-specific work plans or issued as addendum to the generic SAP and approved by USEPA Region 2 and NYSDEC. Changes to the original SAP will only be implemented after the revision has been approved.

The quality assurance officer is responsible for revising the SAP. All project personnel should consult the QAO for the most recent approved version of the SAP.

13.2 SAP DISTRIBUTIONS

Table 21 lists all individuals who should get a copy of the approved SAP, either in hard copy or electronic format, as well as subsequent revisions: All the individuals identified in Table 21 will also receive all revisions, addenda, and amendments to the SAP. These individuals are responsible for removing all outdated material from circulation, distributing revised or added material to update any copies within their organizations.

All project personnel performing work related to sample collection, data producing, data assessment, data management, and data utilization should read the applicable sections of the SAP and perform the tasks as described. A project personnel sign-off sheet is presented in Appendix E and all identified personnel should read and sign off on the applicable sections of the SAP before beginning the tasks. Supervisory or oversight personnel are responsible for communicating the requirements of the applicable portions of the SAP to those doing work.

13.3 SAP ARCHIVING

The approved generic SAP and project-specific work plan, including reviewers' comments and responses to reviewers' comments will be archived in the appropriate project file. The files will be retained for the duration of the project or a minimum of five years, whichever is longer, or as dictated by project requirements (if longer than five years).

14.0 SPECIAL TRAINING/CERTIFICATION

Qualifications for quality assurance officer, field analyst, and data validators are specified in Section 3. In brief, field analyst should have: (1) completed a certification course or training by an experienced analyst who has demonstrated proficiency in the method; or, (2) demonstrated the proficiency by correlation of the analyst's results with laboratory confirmation analysis. Data validation will be performed by trained and experienced data validators. The lead validator will have at least two years experience and be familiar with USEPA Region 2 data validation requirements. The quality assurance officer should have the qualifications specified in the NYSDEC guidance.

Field sample collection team should be led by experienced engineer who has demonstrated proficiency in the sampling method. All onsite workers will also be current on their 40 -hour Occupational Safety and Health Administration (OSHA) Hazardous Waste and Emergency Response (HAZWOPER) Certification. All work will be conducted in accordance with the Generic Site-Wide Health and Safety Plan for Seneca Army Depot Activity (Parsons, 2005).

All field personnel performing radiological surveys should receive a minimum 1-hour of radiological safety and fundamental training, as well as a minimum of 24 hours of onsite orientation and technique training. This will include briefing on the risk associated with radiological contaminants. All radiation scanning work onsite will be overseen by a Health Physicist/Radiological Safety Officer (HP/RSO).

All field personnel performing ordnance and explosives (OE) or unexploded ordnance (UXO) work should receive proper training as specified in the Generic Site-Wide Health and Safety Plan for Seneca Army Depot Activity (Parsons, 2005). All personnel on the UXO teams must meet the requirements set forth in the USACE (2001) Data Item Description (DID) OE-025.01, Personnel/Work Standards. UXO personnel will be U.S. citizens and graduates from one of the following schools or courses:

- U.S. Army Bomb Disposal School, Aberdeen Proving Ground, Maryland;
- The U.S. Naval Explosive Ordnance Disposal (EOD) School;
- The EOD Assistants Course, Redstone, Alabama; the EOD Assistants Course, Eglin AFB, Florida; or a DoD-certified equivalent course.

The following subsections detail individual UXO personnel qualifications.

UXO Safety Officer (UXOSO)

The UXOSO shall have the following skills/knowledge:

- The ability to identify fusing, necessary precautions, and fuze condition; i.e. armed, functioned, or armed and functioning; how this condition can or will affect the munition payload should other forces be applied.
- The ability to recognize munition/ordnance types and to determine the hazards and make risk assessments. This includes identifying potential fillers, including those in extremely deteriorated condition; e.g., high explosives, fragmentation, white phosphorous, and chemical warfare material. UXOSO must also be able to determine if munitions can be moved before destroying or if the munitions must be blown in place (BIP); fragmentation radius; and, in the case of chemical warfare material, the potential down-wind hazard along with the engineering controls to mitigate risk.

Senior UXO Supervisor (SUXOS)

The SUXOS will have at least 15 years combined active duty in military EOD and contractor UXO experience, including at least 10 years in supervisory EOD and UXO positions. This individual will have documented experience with and/or specialized training in the type of UXO/MPPEH expected to be encountered. This individual will be a graduate of the U.S. Army Bomb Disposal School, Aberdeen Proving Ground, Maryland, or the U.S. Naval EOD School.

As the most senior UXO qualified individual onsite, the SUXOS directly supervises all daily UXO/MPPEH activities. This individual is responsible for the successful performance of field teams, early detection and identification of potential problem areas, and instituting corrective measures. The SUXOS shall execute instructions from the Parsons site manager; document site conditions; photographically document operations; prepare project reports; and identify efforts to accomplish the statement of work. The SUXOS reports to the Parsons site manager.

UXO Technician III

This individual supervises a UXO team. This individual will have experience in OE clearance operations and supervising personnel and will be a graduate of the U.S. Army Bomb Disposal School, Aberdeen Proving Ground, Maryland; or the U.S. Naval EOD School. The UXO Technician III will have at least 10 years combined active duty military EOD and contractor UXO or material posing potential explosive hazard (MPPEH) experience

UXO Technician II

This individual will be a graduate of the U.S. Army Bomb Disposal School, Aberdeen Proving Ground, Maryland; or the U.S. Naval EOD School. The UXO Technician II may be a UXO Technician I with at least five years combined military EOD or contractor UXO/MPPEH experience.

UXO Technician I

The UXO Technician I will be a graduate of the EOD Assistant Course at Redstone Arsenal, Alabama, Eglin Air Force Base, Florida, or a DoD-certified equivalent course. The UXO Technician I will not perform UXO procedures without the direct supervision of a fully qualified UXO Technician II (or above). A UXO Technician I may become a UXO Technician II with at least 5 years combined military EOD and contractor UXO/MPPEH experience.

UXO Quality Control Specialist (UXOQCS)

The UXOQCS will have experience in UXO/MPPEH clearance operations and supervising personnel. This individual will have at least 10 years combined active duty military EOD and contractor UXO/MPPEH experience. The UXOQCS will have the required quality control training, including at least two years of experience providing QC on similar projects.

UXO Sweep Personnel

Personnel who have received the 40-hour HAZWOPER training will be hired to fill positions on the visual surface sweep teams and the mag & flag survey teams under the direct supervision of a UXO Technician III. UXO sweep personnel will receive on-site training in UXO/MPPEH recognition avoidance and safety.

Laboratory analyst should complete training by the laboratory and with qualifications deemed appropriate by the laboratory. The laboratories selected to perform analyses must be certified under the Environmental Laboratory Approval Program, implemented by the New York State Department of Health, and be capable of providing complete environmental analytical services consistent with USEPA protocols and NYSDEC ASP protocols.

Any other project specific special training should be recorded in the site-specific work plan.

15.0 DOCUMENTS AND RECORDS

All project documents (e.g., generic SAP, audit reports, internal QA/QC memorandums, interim progress reports, final reports) and records (e.g., field records and notes, communication logs) will be organized and kept consistent with the project management plan prepared by Parsons. All project documentation will be filed in the permanent project files. All project files will be maintained for the duration of the project or a minimum of five years, whichever is longer, or as dictated by project requirements (if longer than five years).

All the following files will be archived after the project is complete:

- Approved generic SAP and site specific SAP or work plan (including reviewers' comments, responses to reviewers' comments, addenda, and amendments),
- Sampling collection and handling records (e.g., field notebooks, operational record, global positioning system data, sampling instrument decontamination records, sampling instrument calibration logs, sampling location and sampling plan, drilling logs),
- Laboratory report (including chain-of-custody forms, sample receipt and tracking records including sample tags and shipping bills, case narrative, analytical log books, test method raw data and QC sample records, definitions of laboratory qualifiers, documentation of laboratory method deviations, and electronic data deliverables),
- Laboratory certification and QA manual,
- Computer documentation such as model input and output files as results of code and database test procedures,
- Audit reports/checklists, documentation of internal QA review, and corrective action reports,
- Interim progress reports and final reports,
- Billing receipts,
- Presentations to be made during and after the project,
- Communication logs, telephone logs,
- Documentation of deviation from methods,
- Data review reports, and

- Any other project related documents.

Electronic project files are maintained on a no-fault server and back-ups of project files on to magnetic tapes on the no-fault server are performed on a weekly basis and updated daily, Monday through Thursday.

Laboratory document control procedures shall be consistent with the NYSDEC ASP.

16.0 FIELD SAMPLING PLAN

This section presents a generic FSP, which in specific terms, specifies the requirements and procedures for conducting field operations and investigations at Seneca Army Depot (or Depot). This generic FSP has been prepared to ensure (1) the data quality objectives specified for the Seneca Army Depot are met, (2) the field sampling protocols are documented and reviewed in a consistent manner, and (3) the data collected are scientifically valid and defensible. A site-specific work plan shall be prepared to supplement requirements and procedures for conducting site-specific field operations and investigations for each specific project or task, and shall reference this SAP document as appropriate to prevent repetition of information.

16.1 INTRODUCTION

The National Contingency Plan specifies circumstances under which an FSP is necessary for Comprehensive Environmental Response, Compensation, and Liability Act response actions. For cleanup actions at the remedial investigation/feasibility study stage, the NCP requires lead agencies to develop sampling and analysis plans that provide a process for obtaining data of sufficient quality and quantity to satisfy data needs (40 CFR 300.430 (b)(8)). Such sampling and analysis plans must include a field sampling plan.

Guidelines followed in the preparation of this FSP are set out in the documents below:

- "Guidance for the Data Quality Objectives Process," (QA/G-4) (USEPA, EPA/600/R-96/055, August 2000a).
- "Data Quality Objectives Process for Hazardous Waster Site Investigations," (QA/G-4HW) (USEPA, EPA/600/R-00/007, January 2000c).
- "Guidance for Quality Assurance Project Plans," (QA/G-5) (USEPA, EPA/240/R-02/009, December 2002a).
- "Guidance on Choosing a Sampling Design for Environmental Data Collection," (QA/G-5S), (USEPA, EPA/240/R-02/005, December 2002b).
- "Guidance for Preparing Standard Operating Procedures," (QA/G-6), (USEPA, EPA/240/B-001/004, March 2001c).
- "Guidance for Data Quality Assessment: Practical Methods for Data Analysis," (QA/G-9), (USEPA, EPA/600/R-96/084, July 2000b).

All staff participating in SEDA activities are required to be familiar with this FSP. The FSP shall be in the possession of the field teams collecting the samples. All subcontractors shall be required to comply with the procedures documented in this SAP (including the FSP presented in this section) in order to maintain comparability and representativeness of the collected and generated data.

As discussed in Section 13, controlled distribution of the SAP (including the FSP presented in this section) will be implemented by Parsons to ensure the current approved version is being used. A distribution list is presented in Table 21.

16.2 PROJECT OBJECTIVES FOR FIELD SAMPLING ACTIVITY

This section presents the project objectives for field sampling activity. The subsections present a summary of project data quality objectives, types of sample analysis, and field activities.

16.2.1 Data Quality Objectives (DQOs)

DQOs define the type, quantity, and quality of data that are needed to answer specific environmental questions and support environmental decisions. The development of DQOs for a specific site and measurement takes into account project needs, data uses and types and needs, and data collection. These factors determine whether the quality and quantity of data are adequate for its end use. DQOs are implemented so the data are legally and scientifically defensible. DQOs for this program are described in greater detail in Section 4 of this document.

16.2.2 Sample Analysis Summary

The number and type of analyses will be determined on a per-task basis and will be specified in each site-specific work plan. Types and frequencies of QC samples (MS/MSD, trip blanks, equipment blanks, duplicates, etc.) required for all sampling activities are described in Section 4. Sample containers, preservatives, and holding time for soils/sediments and aqueous samples are provided in Tables 5-A and 5-B, respectively.

16.2.3 Field Activities

Potential field activities at the Seneca Army Depot include installation of system components (e.g., groundwater monitoring wells), test pit investigation and scanning, soil sampling, baseline groundwater sampling and subsequent process monitoring, building sampling, ordnance and explosives (OE) sampling and analysis, indoor air and ambient air monitoring, radioactive material sampling and analysis, investigation derived waste (IDW) disposal. These activities may include the following:

- Excavation;
- Soil boring sampling;
- Field soil screening test;
- Confirmation soil sampling;
- Stockpile soil sampling;
- Groundwater monitoring well installation;

- Groundwater monitoring well development;
- Water level measurements;
- Groundwater sampling;
- Field measurements of groundwater parameters (e.g., pH, turbidity, hardness, temperature, conductance, alkalinity, dissolved oxygen, oxidation-reduction potential, manganese, sulfide, carbon dioxide, ferrous iron);
- Sampling equipment decontamination;
- Aquifer testing;
- Building sampling and analysis;
- Ordnance and explosives sampling and analysis;
- Indoor air and ambient air monitoring;
- Asbestos material sampling and testing;
- Radioactive material sampling and analysis;
- Disposal of investigation derived waste; and
- Record keeping.

Field activities conducted at each site will be described in each SS-WP.

16.3 FIELD OPERATIONS

This section presents protocols for field operations including soil and rock description, site reconnaissance, preparation, and restoration, geophysical surveys, soil boring advancement, groundwater well installation, monitor well development, monitor well abandon, aquifer test, test pit excavation, survey, equipment decontamination, investigation derived waste disposal, and corrective action.

16.3.1 Soil and Rock Description

Lithologic logs of all borings and excavations, including well construction diagrams, must be provided for the Seneca Army Depot activities. Each log must include borehole identification, soil and rock description, sample depths, methods of sampling, sampling date, land surface elevation, borehole/excavation total depth, and test results such as blow counts. Soil and rock description is an important element for the boring logs and this section presents the procedure for field soil and rock description.

16.3.1.1 Soil Terminology

1. Color

The color of the soil is described using color chips attached to the Geotechnical Gauge. The color of the soil when it is wet is the standard for comparison.

2. Texture/Fabric/Bedding/Stratification

Texture is described as the relative angularity of the particles: rounded, sub-rounded, sub-angular, and angular. Fabric should be noted as to whether the particles are flat or bulky and whether there is a particular relation between particles (i.e., all the flat particles are parallel or there is some cementation). The bedding or structure should also be noted (e.g., stratified, lensed, non-stratified, heterogeneous, varved).

3. Burmiester (1958) Terminology/ Modifiers

The following terms are used to further describe soils:

a.	And	Modifier which identifies a proportion of soil which ranges from 35 to 50 percent.
b.	Some	Modifier which identifies a proportion of soil which ranges from 20 to 35 percent.
c.	Little	Modifier which identifies a proportion of soil which ranges from 10 to 20 percent.
d.	Trace	Modifier which identifies a proportion of soil which ranges from 1 to 10 percent.
e.	+ or -	Modifiers to indicate the extremes of ranges defined above, or that a grain size has more or less of a particular size material.

4. Density and Consistency

The density of noncohesive granular soils is classified according to standard penetration resistance. These classifications are provided on the Geotechnical Gauge for sands, and for silts and clays, using standard split-spoon sampling techniques. The blow counts for the middle 1 foot (using a 2 foot long split spoon sampler) are used for the classification of density or consistency.

5. Plasticity

If a moist soil can be rolled into a thread, it is said to have some plasticity. Materials that cannot be rolled in this manner are non-plastic, or have very low plasticity. The degree of plasticity of the soil may be further measured by the ease with which this material may again be remolded. After reaching the plastic limit, the degree of plasticity may be described as follows:

a. High plasticity (CH) - The soil may be remolded into a ball and the ball deformed under extreme pressure by the fingers without cracking or crumbling.

b. Medium plasticity (CL) - The soil may be remodeled into a ball but the ball will crack and easily crumble under pressure of the fingers.

c. Low plasticity (CL, ML, or MH) - The soil cannot be lumped together into a ball without completely breaking up.

6. Moisture

Moisture content is estimated in the field according to four categories: dry, moist, wet, and saturated.

7. Petroleum Hydrocarbons (non-aqueous phase liquid/oil)

The presence of petroleum hydrocarbons (PHC) or non-aqueous phase liquid (NAPL) in soil samples will be described according to the terms described below:

a. No PHC present - The soil does not contain any visible staining or PHC in the soil pore space.

b. PHC staining - The soil contains PHC staining which is visible on soil grains only. The color of the PHC should also be described (i.e., black, brown, etc.).

c. PHC in soil pores - The soil contains PHC on soil grains and in soil pore spaces. The color of the PHC should also be described (i.e., black, brown, etc.).

16.3.1.2 Soil Description

Soils logged during test pit activities or recovered from soil and bedrock borings will be classified according to the ASTM D2487-92, Standard Classification of Soils for Engineering Purposes (Unified Soil Classification System), with descriptive text added to the Unified Soil Classification System (USCS) following the procedure outlined by the Burmister (1958).

The following procedure specifically addresses the description of samples using split-spoons in association with drilling operations.

1. Measure, or observe the drilling crew measure, all parts of the drilling equipment that will affect the depth of the sample. These include the length of the drill bit, auger bit, any drilling subs, the length of the split spoons and sampling head, etc. The field crew must be cognizant of the depth of the drill hole and associated equipment at all times.

2. Soil samples will be retrieved from drilling operations as described in Section 16.4.2.

3. Immediately after opening the split spoon sampler, the contents of the sample will be screened for VOCs using a Flame Ionization Detector (FID) or Photoionization Detector (PID). The data will be recorded in the appropriate locations on the Boring Report Form. Readings will be taken at one to three locations along the split spoon sample with additional readings taken if additional distinctive zones are observed.

4. Split the sample length-wise to expose a clean sample face for classification of stratigraphic features and for sample collection.

5. Determine soil descriptions using a Geotechnical Gauge. Record descriptions on the Boring Report form or Test Pit Record form using the following order and format: Test pit soil description will be based on a clean view of the sidewall of a test pit.

    - Color (while wet);
    - Grain size;
    - Major soil component descriptor (CLAY, SILT, SAND, GRAVEL, PEAT), with modifiers as applicable (micaceous, fibrous, etc.);
    - Other components in decreasing order using the Burmister Classification System to quantify amounts (and, some, little, trace with + or - as applicable);
    - Density from blow count data (if split spoon);
    - Other descriptive modifiers such as stratification, plasticity, staining, minor minerals (if recognizable), unique materials or features, and odor (if present);
    - Moisture content (if the drilling method used does not interfere with the sample moisture and if the sample is above the water table) and presence of NAPL;
    - Possible origins will be given if enough information is available (i.e. fill, alluvium, till, glacio-marine, etc) on the next line after the soil description in parentheses;

- In some areas, the soil (clay, silt, sand, peat) may only be a minor component to foreign debris. If this is the case, the field personnel should note down the approximate percentages of debris vs. soil;
- General debris types; and
- Cross sections of the excavation for test pits or trenches.

The following is an example of an acceptable soil description:

Light brown, coarse to fine micaceous SAND, some - Silt, little + coarse + Gravel, medium dense, well graded, weakly stratified showing grade bedded, minor iron-oxide stain on quartz grains, dry. (Alluvium)

Note: Acronyms and abbreviations may be used to save space on the log forms. Abbreviations and acronyms should be minimized to avoid confusion.

6. Descriptions of the soil contained in the sampler will be made while the soil remains in the split spoon sampler.

7. Record the penetration interval of the split spoon sampler on the log form.

8. Record the sample recovery of the split spoon sample on the log form. While determining the length, care must be taken to measure only material that represents true sample. Discount material that may be wash or slough material in the spoon. If recoveries fall below 25 percent (e.g., 0.5 feet from a 2 foot sampler), the driller must make alterations to his sample collection methods to improve recovery. Alterations must be approved by the Site Manager before they are implemented. Such alterations may include modifications to the sample catcher, driving a spoon or core barrel beyond its length to pack the sample tighter within the spoon, or changing the diameter of the split spoon or core barrel. If more soil volume is needed for physical or chemical determinations, a 3 inch diameter split spoon may be used in place of the standard 2 inch diameter spoon. All deviations from the standard 2 inch diameter by 2 foot long split spoon should be recorded on the Soil Boring form.

9. Collect a representative and continuous portion of the sample and place it in a glass sample jar. Jar size will be determined prior to field operations. Collected soil materials may subsequently be used as a reference sample or for other physical characterization and screening purposes.

10. Record the interval (i.e., location within the recovered split spoon) of the sample on the field log.

11. Visually estimate, based on sample recovery and blow counts, the range of recovery for the sample. For shallow sample intervals, a segment of the interval may not be represented due to cobbles

obstructing (possibly indicated by higher blow counts) the tip of the spoon. In deep sample intervals residing below the water table, the deepest portion of the sample may have been washed out of the tip of the spoon due to a faulty ball valve at the top of the spoon or a worn sample catching basket.

12. Any deviation from standard drilling procedures and the applicable depth will be recorded in the main body of the log form or in the REMARKS section. Such things as modifications to the sample methods to improve recovery, or changes in the drilling method must be recorded. In particular, record sections where there was no attempt to collect a sample or where a roller bit or some other method was used to advance the hole.

16.3.1.3 Rock Description

Bedrock descriptions are dependent on the classification of the rock types present (igneous, sedimentary, or metamorphic). The rock materials retrieved during coring operations will be described on the Core Boring Report (Appendix C), as applicable, using the following parameters:

- Color - The overall color of the rock, not a particular mineral;
- Grain Size - The size of crystals or clasts making up the rock;
- Texture - This applies only to igneous and some metamorphic rocks, and pertains to whether the rock is crystalline or glassy, equigranular, or porphyric in nature;
- Major Minerals – This applies to the identifiable minerals present as necessary as modifiers to the rock type, i.e. mica Schist, feldspathic Granite, quartz-mica Gneiss;
- Rock Type - Granite, Gneiss, Amphibolite, Argillite, Sandstone, Limestone, Greywacke, etc;
- Bedding and/or Foliation - Describes lineations within the rock. i.e. massive, poorly foliated, well bedded, cross-bedded, etc. The description in the log will include at least an approximate angle of any foliation or bedding, if present;
- Continuity - Joints and fractures, or the lack of, in the rock, cross-cutting veins of materials different from the primary rock type. Fracture, vein, and joint angles will be referenced to the foliation. The openness of any fracture or joint will be evaluated based on core recovery, weathering, fracture density, etc.
- Competence - The weathering features of the rock. Weathering features, combined with rock type and continuity, will give the overall hardness of the rock; and
- Other - Secondary minerals, folding features, etc.

Both the overall core length as well as individual pieces of core (greater than 4 inches in length) will be measured. The data are used for the calculation of Rock Quality Designation (RQD) factors and for the interpretation of fracture spacing. Core recovery will be recorded in two manners: as the ratio of core recovered to length of core run; and, as a percentage recovery (i.e. 3.5 feet of 5.0 feet cored, 70%). The RQD will be calculated by: 1) summing the length of all the pieces greater than or equal to 4 inches in length recovered in the core barrel; and 2) by dividing this sum by the cored interval length. The resulting value will be expressed as a percent and recorded in the Core Boring Report (Appendix C).

16.3.2 Site Reconnaissance, Preparation, and Restoration Procedures

Parsons will contact Under Ground Facilities Protection Organization (UFPO) at 1-800-962-7962 prior to any earthwork operations, trenching, or excavation. Areas designated for intrusive sampling shall be surveyed for the presence of underground utilities. Utility locations are determined using existing utility maps, and in the field, are verified using a hand-held magnetometer or utility probe. SOPs for utility line identification and drilling and excavation are presented in the Generic Site-Wide Health and Safety Plan (Parsons, 2005). A pre-drilling checklist is attached in Appendix C. Field personnel should consult the project manager and finish the checklist before any intrusive activities. Parsons will notify the Army the planned locations of intrusive activities the Army's approval is warranted before any intrusive activities. A notification letter will be submitted to USEPA and NYSDEC one month before site activities such as intrusive activities and sampling activities. Vehicle access routes to sampling locations shall be determined prior to any field activity.

It should be noted that no construction work will be permitted during the 9 days of the annual deer harvest. Dates for calendar year (CY) 2004 are November 22, 26, 27, December 1, 3, 4, 8, 10, and 11. Dates for CY 2005 and beyond have yet to be determined. Construction work can be conducted any other time of the year. During the construction period, Parsons will notify the COR at the end of each week, what work is planned for the following week. The COR may stop work at any time when an imminent danger/serious safety violation is found.

A centralized decontamination area shall be provided for drilling rigs and equipment. The decontamination area shall be large enough to allow storage of cleaned equipment and materials prior to use, as well as to stage drums of decontamination waste. The decontamination area shall be lined with a heavy gauge plastic sheeting, and designed with a collection system to capture decontamination waters. Solid wastes shall be accumulated in 55-gallon drums and subsequently transported to a designated waste storage area. Smaller decontamination areas for personnel and portable equipment shall be provided as necessary. These locations shall include basins or tubs to capture decontamination fluids, which shall be transferred to a large accumulation tank as necessary. The designated areas of decontamination shall be specified in the SS-WP.

Parsons field office will be located in Building 125 at the Depot, unless otherwise specified in the SS-WP.

Each work site or sampling location shall be returned to its original condition when possible. Efforts shall be made to minimize impacts to work sites and sampling locations, particularly those in or near sensitive environments such as wetlands. Following the completion of work at a site, all drums, trash, and other waste shall be removed. Decontamination and/or purge water and soil cuttings shall be transported to the designated locations as described in Section 16.3.12.

16.3.3 Geophysical Surveys

General requirements for all geophysical surveys are: (1) the geophysical surveys should be supervised by a state licensed geologist or engineer, (2) the locations of boreholes logged with geophysical instruments shall be shown on a site map, (3) the locations of surface geophysical grid system layouts shall be shown on a site map, (4) the location of areas analyzed with subsurface geophysical techniques shall be shown on a site map (5) final results shall be presented in plan views and cross sections. Contours shall be used where appropriate, (6) the survey report shall present survey results as well as limitations of the method and data and, (7) the interpretation of the data shall be incorporated into the conceptual site model. Geophysical surveys at potential OE/UXO sites are discussed in Section 16.3.14.

16.3.3.1 Electromagnetic (EM-31) Survey

Electromagnetic (EM) -31 surveys may be performed at the Depot. The objectives of the EM-31 surveys will be to delineate waste boundaries, identify the location of buried metallic objects, and identify the locations of old disposal pits. The EM-31 method will typically be employed in conjunction with Ground Penetrating Radar (GPR) surveys so as to provide significant redundancy during the geophysical investigations.

16.3.3.1.1 EM-31 Survey Procedures

The electromagnetic data will be collected using both grid and profile based surveys. In general, the grid based surveys will use either a 10 foot by 10 foot or 20 foot by 20 foot grid spacing. The corners of the geophysical survey grids will be established using a registered NY State land surveyor. The individual EM-31 survey lines and station locations will be established using both hip chains and hand held compasses.

At the site where EM-31 data will be collected, a data logger will be used to record the individual electromagnetic readings. Both the in-phase and quadrature components of the electromagnetic field will be measured and recorded. Readings will be measured both parallel and at 90^{o} to the transect line

if the orientation of anomalies is required. These data will in turn be stored on a computer and printed out at the end of each field day. For each site where EM-31 survey is to be conducted, a calibration area, free of cultural interference, will be established. The EM-31 response will be measured at this area at the start of each day. This check will be made every 2-3 hours throughout the survey to insure that no significant meter drift is occurring during each survey.

16.3.3.1.2 Data Interpretation

Upon completion of each electromagnetic survey, the data will be presented in both profile and contour form. Both the in-phase and quadrature components will be plotted. This multiple presentation format will aid in the interpretation of the data. All of these presentation aids will be interpreted to identify the locations of buried metallic objects, disposal pits, waste boundaries, and areas of elevated subsurface soil apparent conductivities. These data will be compared to the results of the GPR surveys to provide as complete and accurate interpretation of the subsurface conditions at each SWMU as possible.

16.3.3.1.3 Data Verification

The EM-31 instrument is calibrated by the manufacturer. This calibration can be rechecked in the field but this requires that access to highly resistive rock outcrops are available. A secondary field calibration is performed on a daily basis to insure repeatability of measurements and to check against daily meter drift. This field calibration is the only performance evaluation that is performed on these instruments.

16.3.3.2 Electromagnetic (EM-61) Survey

Electromagnetic-61 surveys may be conducted with the Geonics EM-61 High-Sensitivity Metal Detector at the Depot. The objective of the EM-61 surveys is to identify the location and depth of buried metallic objects, including UXO, utility lines, underground storage tanks, and waste disposal pits. The unit is capable of detecting a single drum at a depth of about 10 feet. The EM-61 utilizes time-domain electromagnetic principles to provide higher resolution and rejection noise than the frequency-domain EM-31. However, the EM-61 is not well-suited to map shallow groundwater contamination or changes in surficial geologic materials.

16.3.3.2.1 EM-61 Survey Procedures

1. Grids will first be established and the corners of each EM-61 grid will be established by a registered NY State land surveyor. Additional temporary markers or flags will be placed for control within the grid.

2. Grids will be surveyed by the EM technique using Geonics EM-61 TDMD instruments. Parsons personnel will conduct these surveys. The device consists of a one-meter square transmitter/receiver frame, an electronics backpack, and a hand-held data logger. The frame houses two coaxial coils: one 40 cm above the other. EM-61 devices generate electromagnetic pulses that trigger eddy currents in the subsurface. The eddy current decay produces a secondary magnetic field that is monitored by two receiving coils and recorded by an attached data logger. For the most part, the EM-61 instrument will be used in a wheeled mode. The survey can be conducted by driving the cart over the targeted area. In this case, the survey will require two operators on board during data acquisition, which consists of one driver and a passenger to assist with navigation and monitor incoming data on the laptop. Alternatively, in rough terrain, the wheels are removed and the transmitter/receiver frame may be carried by the operator. A second individual will record the progress of the survey as well as any surface features that might affect the response of the instrument. Detailed record keeping will facilitate the discrimination of surface and subsurface objects. This person will also place survey markers to allow the EM-61 operator to maintain accurate profile lines.

3. EM-61 data will be collected along parallel survey lines spaced 3 feet apart in all grids with dimensions of 100 ft by 100 ft. Review of the Geophysical Prove-out Report data indicated that a survey line spacing of three feet is required to detect OE the size of an MKII grenade or smaller. Prove-out results also show that OE the size of a 155mm shell buried four feet below the ground surface will be detected up to four feet away from the center of the EM-61 sensors. If larger lane spacing than those stated above are believed to be warranted for a particular area, the justifications for such changes will be provided to the Parsons project manager and USACE. Any such changes will be considered on a case by case basis, and will be approved by the Geophysical Coordinator, the Parsons project manager, and USACE prior to implementation in the field. Discrete measurements are taken every 8 inches along the profile lines. Measurements are automatically triggered by the survey wheel and stored in the data logger. The voltages (mV) induced in both receiver coils are recorded at each station.

4. Grids surveyed manually, using the EM-61 in the single unit configuration, will be subdivided into parallel survey lanes. During the EM-61 survey, the survey lines are traversed over a known distance with data being collected incrementally with distance. EM measurement events are triggered each time the instrument's tire rotates a specified distance. Data markers (fiducial marks) can also be inserted manually by the operator. Review of the Geophysical Prove-out Report data indicate that only a single fiducial mark will be needed at every 50 feet of each manually surveyed line to meet the lateral positioning accuracy goal of ±1 foot established for this project.

5. Data corrections for data collected manually will be performed using information recorded in the field log books (start and end of line stations, line spacing, fiducial mark intervals, etc.),

information digitally recorded in each EM-61 data file, and the geodetic survey coordinates of the grid corners. This operation involves correcting the EM-61 data that was collected incrementally with distance to either compress or expand the recorded measurement locations for each line so that they cover the actual distance traveled. This operation is required to compensate for variations in the terrain along the survey line, which affects the rotation of the instrument's wheels. The survey data are then rotated and translated from the local coordinate system they were collected in (where the southwest corner of the grid surveyed was assigned a coordinate of 0E, 0N) to the New York State Plane coordinate system.

6. A "meandering path" geophysical survey will be conducted in areas where grids cannot be cleared by randomly traversing investigation areas using EM-61 units in conjunction with Trimble® 4800 GPS units. The EM-61 and 4800 instruments will be set up and checked following the procedures in the provided instruction manuals. The EM-61 unit will be manually towed by one of two individuals comprising the geophysical survey team. Each team will be assigned a UXO escort to provide visual OE clearance of the transect path and brush cutting as necessary. The lengths and locations of these transects may change depending on field conditions. The area covered by a transect will be calculated as the distance traveled multiplied by the width of the EM-61 footprint (one meter).

7. The Pathfinder™ software (provided by Trimble®) will be used to determine times of the day during which the correct number and position of satellites cannot be obtained. The daily work schedule of download and survey times will be appropriately adjusted to account for these times.

8. During the surveys, the EM-61 will collect EM data while the GPS records the location of the data collection points. EM-61 data will be time-stamped and combined with the GPS positioning data. If GPS lock is lost during the geophysical survey, an audible signal notifies the geophysicist of the condition. If the signal is not reacquired within a few seconds the survey is temporarily halted until the signal is again locked. In addition, the geophysicist may opt to begin walking a straight line segment at constant pace upon indication of loss of GPS lock so equipment position can be reconstructed by a time average across the distance lost until GPS lock is again obtained. As a worst case, very small data segments in the transect may be lost. This very small data loss is inconsequential as the transects are typically lengthened during the survey in anticipation of this minor loss. If the lost signal is not reacquired within a few minutes, the geophysicist may move a distance away from the last survey location and recommence survey at a new location, thus breaking the transect into smaller pieces.

16.3.3.2.2 Data Interpretation

Upon completion of each EM-61 survey, the data will be presented in both profile and contour form as a check of data quality and completeness. After correcting for bias or offset in each data set, the response from the lower coils will be presented as color contour maps to facilitate interpretation. The difference in the response of the upper and lower coils may be used to estimate the depth of each anomaly. The EM-61 data will be compared to the results of other geophysical surveys to provide a comprehensive interpretation of subsurface conditions.

16.3.3.2.3 Data Verification

The EM-61 is calibrated by the manufacturer. There is no means or necessity to calibrate the instrument in the field. The functionality of each instrument is tested daily by passing the EM-61 over a known metallic object and noting the response. The background response of the EM61 may vary slightly from day to day or from instrument to instrument. However, post-processing of the data removes this bias. Interpretation of EM-61 data requires only the relative response of each receiver coil.

16.3.3.3 Ground Penetrating Radar Survey

A GPR survey of selected areas within the depot may be conducted to locate buried structures (i.e., buried or filled-in pits, trenches, disposal areas) and obtain more information on anomalies detected during the electromagnetic surveys. GPR can also identify the original ground surface beneath berms.

16.3.3.3.1 GPR Survey Procedures

The GPR instrument will be hand operated on the identified areas. As the equipment is pulled across the site, the reflected radar pulses are transmitted to the receiver unit where they are converted to analog signals. The analog signal is transmitted to the control unit where the signal is electronically processed and sent to the graphic recorder. The graphic recorder produces a continuous chart display on electro-sensitive paper. This real-time display enables the operator to interpret the data on site.

16.3.3.3.2 Data Verification

Data from the GPR survey will be verified when subsurface explorations are performed to identify anomalies and penetrate through disposal pits.

16.3.3.4 Exploration of Subsurface Geophysical Anomalies

Exploration of subsurface geophysical anomalies will be performed to verify the data obtained during the GPR and electromagnetic surveys.

The excavations will be performed using a backhoe with a smooth-edged bucket. The excavation will extend to a distance of five feet on either side of the subsurface anomaly. The width, length, and depth will be based on the size of the geophysical anomaly with applicable considerations for prevailing conditions such as flooding or stability of the excavation. Based on consultation with the project manager and field team leader, the final depth of excavation will be decided. The boom and bucket of the backhoe will be operated in such a manner as to not exert impact or shock to the soil or its contents. The depth of the excavation increment (not to exceed two feet) will be at the discretion of the UXO Safety Officer. The contents of each bucket of material removed from the excavation will be gently placed on the ground and spread out to expose the contents as much as possible for a visual inspection. If at any time during the excavation, the UXO Safety Officer determines the risks and hazards are too great to proceed with the excavation, the excavation will be halted.

The excavation will be continuously monitored with a PID or organic vapor monitor (OVM). At no time will any personnel be permitted to enter the excavation. If the pit is not closed immediately after any samples have been obtained, the excavation will be barricaded to prevent accidental entry by personnel working on the site. Each excavation will be marked after closure as needed for identification of the site.

A log containing the location of each excavation will be maintained by the field team. The log will include the excavation number, location, items observed (such as UXOs or drums), and other significant data. Records pertaining to sampling, geological data and associated requirements will be maintained by the project geologist.

Sites that potentially contain UXOs will be investigated by a UXO technician with the aid of UXO Safety Officer and UXO Project Leader. Due to the potential hazards associated with the excavations, when necessary, the UXO contractor will obtain samples for the project geologist in accordance with the sample collection procedures described in Section 16.4. The excavation equipment will be cleaned between excavation sampling operations in accordance with decontamination procedures outlined in Section 16.3.11.

16.3.3.5 Geophysical Survey Methods-Magnetics

In the case of grids placed in areas where the maneuverability of the EM-61 instruments is too limited to enable accurate data positioning or in areas where identification of a number of anomalies suggests using another method to improve anomaly picking, a Geometrics G-858 magnetometer (or equivalent)

may be used for the surveys, except in areas where slap flares are expected. The G-858 instrument uses a cesium vapor magnetometer sensor incorporating a miniature atomic absorption unit from which a signal proportional to the intensity of the ambient magnetic field is derived (Pawlowski, et. al., 1995). The sensitivity of the instrument ranges from 0.05 nanoTesla (nT) at a data recording rate of 10 Hz to 0.01 nT at a data collection rate of 1 Hz. An operational manual of the G-858 is attached in Appendix G.

Data collected with a G-858 will use the same procedures for grid preparation and data processing as those for the manually-towed, single unit EM-61 configuration described above. The G-858 is carried by the operator above the ground, while the EM-61 is rolled along it. In addition, it requires less than two feet of lateral space while the EM-61 requires three. This means that the G-858 can sometimes be used in areas where the EM-61 cannot, especially in wooded or hilly areas. The vertical separation of the coils will be set at 1.5 feet for all surveys. For the most part, it is expected that bottom sensor data will be used to make target picks. However, gradient or top sensor data may be used in regions where large ordnance is expected, as either may exhibit less noise than the bottom sensor in high clutter areas.

The magnetic technique will also be applied using Schoenstedt™ GA-52CX or White's, which also detect non-ferrous metals, magnetometers to pinpoint the exact locations of anomalies as part of the intrusive investigation for hilly or very heavily wooded areas. Size and orientation of buried targets and the soil characteristics of the work area limit the depth of detection of either of these magnetometers. Neither instrument is not capable of classifying the anomaly; each will only show the presence or absence of a magnetic field.

16.3.3.6 Geophysical Survey Instrument and Equipment Maintenance and Inspection

Testing Procedures and Frequency

Instruments and equipment used to gather and generate environmental data will be tested with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications.

Hand-Held Metal-Detector QC

At least twice daily, all of the hand-held metal-detectors (White's, Schonstedt™) will be function checked at a test grid to be established at the beginning of the project. The checks will be performed by measuring the instrument response over locations of items in this test grid and comparing that response to the standard response of each instrument. The seed items in the test grid will be inert or simulated items representing an M-9 grenade buried at 2 feet and a 155 mm shell buried at 4 feet. In addition, a slap flare, a 40 mm grenade, and a fuze (or reasonable simulants) will be seeded at depths to be chosen as representative of those expected at the areas of concern. The ability of the metal-detector to detect

the items is the only pass/fail criteria in this QC check. If the instrument cannot detect all of the items, it will be removed from service.

EM-61 and G858 Daily QC

Prior to beginning grid surveys, a baseline spike reading will be determined for both the EM-61 and the G858. Each instrument will be used to collect 10 survey lines over a metal spike placed in the ground. The range between the minimum and maximum readings for each line will be averaged to determine the baseline reading for each instrument. During each subsequent day of use, the EM-61 and G858 magnetometer will be tested before and after the survey of each grid block. A metal spike will be placed in the ground adjacent to each of the grids, and one survey line will be collected over this spike before and after the survey of the corresponding grid. The instrument response over the spike will be recorded on a survey sheet, and the highest readings for each line will be compared to the baseline spike value for the corresponding instrument to ensure that the instrument response is consistent. Peak readings within 20% of the baseline reading will be regarded as consistent for the purposes of QC.

A static test of the EM-61 and the G858 will be performed each morning in order to detect any drift occurring in the instrument's response over a short time period. Cables will be shaken to test for shorts, and loose cables will be taped to the appropriate sensor frame. Each instrument will be set to collect data continuously for three minutes (4 readings a second for the EM-61 and 10 readings a second for the 858) over one location. Afterwards, a small metallic test object will be placed on the same location in a standard orientation, centered beneath the instrument sensors, and the static test will be repeated. For this project, a metal spike (or an inert M69 if possible) will be used as the test object. If the response of the instrument varies on either test by more than ±3mV of the initial response for the EM-61 or ±3nT on the gradient scale for the G858, the instrument will be repaired or removed from service. Data will be graphed and examined for compliance with the required QC guideline and documented in a daily field logbook.

In the case of the G858, a file will also be collected each day in order to correct any heading errors associated with the collection of magnetic data. This file will consist of a continuous measurement of one point. The operator will hold the magnetometer sensors over this location and turn in a 360° circle around the location. As the operator turns through each point of the compass (N, S, E, and W) a mark will be made in the data. Any variation in the magnetic field strength identified in this file will be attributed to the direction that the operator was facing at the time and will be processed out of the final data set.

Finally, one line of each grid block collected, typically the first line, will be repeated after collection of the grid. For each grid, the QC line will be collected first, a new file will be established to collect the

remainder of the grid, and a third file will be used to re-collect the QC line upon completion of the grid. The QC lines will then be graphed and compared to ensure that they overlay each other.

EM-61 and G858 Weekly QC

Once a week, a more detailed QC check will be performed on each of the instruments. For this QC, a 100-foot long line will be established near the site trailer. For each instrument, six survey profiles will be collected along this line. The six profiles will be collected as follows:

1. Profile 1 will be run approximately N or E with no added anomalies along the line,
2. Profile 2 will run the opposite direction with no added anomalies along the line,
3. Profile 3 will run N or E with a spike added at the 50' mark along the line
4. Profile 4 will run the opposite direction with the added spike on the line
5. Profile 5 will run N or E at a very fast pace with the added spike on the line
6. Profile 6 will run the opposite direction at a very slow pace with the added spike on the line

Background repeatability will be established by a comparison of the first two profiles, anomaly repeatability will be established by a comparison of profiles 3 and 4, and proof of acquisition speed insensitivity will be established by a comparison of profiles 5 and 6. For QC, the first two lines should match each other to within ±3mV for the EM-61 or ±3nT on the gradient scale for the magnetometer, and the peaks on the anomaly-included profiles should be within 20% of each other.

GPS QC

For the purposes of grid location and anomaly reacquisition, the GPS equipment will be tested at known survey monuments. A GPS point will be collected at an established survey monument at the beginning and end of each day. Stations measured to within 0.5 feet of the known location of the survey point will be deemed accurate for the purposes of this project. For meandering path QC, two spikes will be placed in the ground in the vicinity of an existing survey monument. When geophysical data is to be collected in the meandering path mode, the GPS will be used in conjunction with the EM-61, and a line of data will be collected over these two points and the survey monument to ensure that meandering path data can be used to correctly locate anomalies. These three points will remain constant throughout the project. A "lag bar" or similar piece of metal will used in all meandering path surveys to post-process and locate the data correctly. All of the QC data collected during the project will be submitted with the survey data collected on the corresponding day. In the case of meandering path QC data, both raw and corrected ASCII files will be submitted. Any processing or filtering of the data will be detailed in a readme.txt file sent with the data.

Testing, repair, or replacement records will be filed and maintained by the Geophysical Survey Team Leader and Intrusive Investigation Field Supervisor and may be subject to audit by the QA Manager.

Testing records of the field instrumentation will be filed with the Parsons project manager in Boston after the field work is completed.

Field Instruments

All geophysical survey instruments will be function checked twice daily as described above. The operational and test procedures will conform to manufacturer's standard instructions. This field test will ensure that the equipment is functioning within the allowable tolerances established by this project.

16.3.4 Soil Boring Advancement

Soil boring procedures will be performed following industry standards. Unless otherwise directed by the project manager, the borings will be advanced to "refusal" which will represent the depth of the "competent" bedrock. Auger "refusal" in "competent" shale will be defined as the depth (after penetrating the weathered shale) when augering becomes significantly more difficult and auger advancement is slow.

16.3.4.1 Equipment

- Drilling rig capable to drilling to the appropriate depth for the well
- 4 1/4-inch or 6 1/4-inch I.D. hollow stem augers (HSA)
- Split Spoon Samples: 2-inch and 3-inch, 2-foot-long carbon steel split spoons
- FID or PID (e.g., OVM)
- Folding ruler
- Field table
- Tin foil
- Ball jars with lids
- Field book
- Boring log field forms
- Laboratory sample containers
- Coolers
- Ice
- Stainless steel spatula
- Stainless steel sample bowls
- 55-gallon drum for soil
- Decontamination equipment as described in Section 16.3.11.
- Level D health and safety equipment as described in the Generic Site-Wide Health and Safety Plan.

16.3.4.2 Field Procedures

1. Pre-drilling check as described in Section 16.3.2.

2. Inspect all drilling equipment.

3. Decontaminate all drilling equipment (e.g., rig, water tank, casing, augers, rods, tubs, tools, etc.) as per Section 16.3.11 prior to starting the work. Inspect all equipment to assure that residual oils, asphalt, grease, grout, soil, etc. has been removed.

4. Go to the boring location and use hollow stem augers method to initiate the boring. Where site conditions (e.g., fine sand running up into the augers) prevent the use of augers, soil borings may be advanced using the drive and wash technique, with the approval of the project manager.

5. Any water used during drilling will be clean potable water that has undergone water quality analyses. The amount of water used will be kept to a minimum, with the estimated amounts used on any boring recorded on the boring logs. **No other drilling additives shall be used**.

6. Alternative drilling methods may be allowed when approved in writing by the Parsons project manager, the Army, or the Regulatory Agency.

7. Use of lubricants is subject to the approval of the Parsons project manager, or the field team leader. If lubricants are used on down-hole equipment they must be non-petroleum based products. Material Safety Data Sheet (MSDS) describing the product must be provided to Parsons project manager in advance of use. In addition, Parsons may require that a comprehensive chemical analysis of the lubricant be completed prior to use.

8. Care will be taken to avoid contact between downhole drilling equipment and those parts of the rig where petroleum based lubricants are used (i.e., motors, hydraulic lines and pimps, transmissions, gearboxes, etc.).

9. Boreholes will be advanced to a predetermined depth or refusal. For temporary well installations, advance the boring to a point immediately above the targeted sample interval (i.e., screened interval). The final depth of the borehole will be verified by the field crew.

10. Split-spoon refusal is defined as the point where 100 or more blows of the hammer fails to advance the split spoon sampler more than 6 inches.

11. During drilling, soil spoils will be continuously monitored for volatile organic compounds. Monitoring specifications are described in the Generic Site-Wide Health and Safety Plan.

12. Spoil materials will be removed from the vicinity of the borehole mouth periodically throughout drilling. Spoils associated with grouting operations will be handled as a waste stream.

13. Mark the boring with a stake or flagging so that it's location can be surveyed and label the stake or flagging with the boring number.

14. Samples shall be collected in accordance with procedures outlined in Section 16.4.

15. After the boring is completed, and if a well is not to be installed, it shall be refilled to the ground surface with lean grout containing at least 3% bentonite powder by volume. The cement/bentonite grout seal shall be placed from the bottom of the boring to approximately 3 feet below ground surface by pouring the mixture into the hole. The grout mixture shall consist of Portland cement (ASTM C 150-86) and water in the proportion of not more than 7.0 to 8.0 gallons (gal) of clean water per bag of cement [1 cubic foot (ft^3) or 94 pounds (lb)]. Additionally, 3 percent by weight of bentonite powder will be added to help reduce shrinkage of the grout mixture. The grout will be allowed to set for a minimum of 48 hours. If the borehole is greater than 15 feet and groundwater is present in the borehole, the grout will be pumped through a tremie pipe to the bottom of the boring. Grout will be pumped in until undiluted grout discharges from the bore hole at the ground surface. A bentonite backfill consisting of bentonite pellets will be placed from the top of the cement/bentonite grout seal to the ground surface and allowed to hydrate.

16.3.5 Groundwater Monitoring Well Installation

This section presents installation SOPs for unconsolidated groundwater monitoring wells and bedrock groundwater monitoring wells.

16.3.5.1 Unconsolidated Groundwater Monitoring Wells

Proper design, construction, and installation of the proposed monitoring wells are essential for accurate interpretation of the groundwater data. The program to be implemented is consistent with the USEPA Region 2 CERCLA QA Manual and the NYSDEC TAGMS regarding design, installation, development and collection of groundwater samples. Further, the program is in compliance with all requirements described in the NYSDEC, 6 New York State Codes, rules and Regulations (NYCRR) Part 360, Solid Waste Management Facilities Regulations, Section 360-2.11, which details groundwater monitoring well requirements. All details of the well completion activities will be recorded on the Overburden Monitoring Well Completion Report & Installation Detail form (Appendix C).

16.3.5.1.1 Equipment

- A 4 1/4-inch or 6 1/4-inch hollow-stem auger

- 4-inch, 6-inch, or 8-inch diameter, Schedule 40 or 80 polyvinyl chloride (PVC), threaded, flush jointed, PVC wire-wrapped well screen (5 and 10 foot lengths) of appropriate slot size (expected screen slot size of 0.010"), riser pipe, threaded end cap, and expansion plug for top of riser.
- Portland cement
- Powdered bentonite
- Filter sand pack
- Fine filter sand (No. 00)
- Bentonite chips, preferably Enviroplug brand
- Protective casing or a roadway box, as directed.
- Metal stamps to label casing and roadway boxes.
- Potable water
- Tremie pipes for sand, seal, and grout
- Overburden Monitoring Well Completion Report & Installation Detail form (Appendix C)

16.3.5.1.2 Procedure

1. Overburden borings will be advanced as described in the Section 16.3.4.

2. Equipment decontamination as described in Section 16.3.11. All equipment must be steam cleaned between holes. Where possible, upgradient wells should be drilled first. Water used during drilling or well installation will be clean potable water that has undergone water quality analysis. Estimated amounts of water used will be recorded on the appropriate forms.

3. Installation of overburden monitoring wells will begin as soon as possible following the completion of the boring. Once installation of the well has begun, the installation process must be continuous until the well has been grouted and all augers or casing removed. Only one well will be installed in each boring. Installation will begin within 48 hours for fully cased boreholes. Once installation has begun, no breaks in the installation process will be made until the well has been grouted and the drill casing removed. In some instances installation of well clusters (i.e., overburden and bedrock wells) may be required. The number of wells at a sampling location will depend on the heterogeneity and simplicity of the geology, the physical/chemical properties of the contaminants, and the location of the suspected sources of pollutants.

4. If well installation does not begin immediately after borehole completion, steps must be taken to insure the integrity of the borehole. Such steps include securing the top of the drill pipe to avoid downhole contamination and to prevent vandalism (e.g. cap and block the hole using the drill head, alternatively block access to the outside of the drill pipe using a drum and blocking it with the drill head).

5. Depending on stratigraphic conditions, all boreholes should be over drilled by a distance of 0.5 feet to 1 feet to allow for the installation of a sand cushion at the base of the well's screened length. The amount of over drilling must be confirmed by the field team leader prior to installation of the well.

6. When using drive-and-wash or other drilling methods requiring water, the casing must be flushed prior to well installation to remove residual overburden material.

7. The Parsons field crew will measure, or observe the driller measure, the depth to the bottom of the borehole. Confirm that the depth is sufficient to proceed with well installation or direct that additional drilling be conducted to reach the required depth. Record the bottom of boring depth on the Installation form prior to proceeding with the well installation.

8. The project manager or field team leader will define the well screen length, slot size, and type of surface completion required for the well installation. Wells will generally be screened from 3 feet above the water table to the top of competent bedrock.

9. Verify and record the actual length and slot size of the well screen and the effective length of the point of well plug or cap that will be used to construct the well prior to beginning the installation.

10. All PVC well materials must be new, clean and in the manufacturer's wrapping. Check the condition of each piece before it is placed in the hole. Any well component that is not found to be visually clean and free of soil or grease will either be decontaminated prior to use or replaced. Decontamination will consist of steam cleaning as defined in the SOPs, and if steam cleaning does not remove contamination, the well materials will be replaced.

11. Verify that materials at the drill site are the correct size or brand and present in sufficient quantity to complete the installation without interruption. If necessary materials are lacking, postpone installation of the well until required material is present. Essential materials include well screen, riser, well point, expansion plug, filter sand, bentonite chips, bentonite powder, and Portland cement.

12. Thread the well point plug or cap onto the screen. At the well head carefully lower the well assembly (screen/well point first) into the borehole, attaching additional sections as the well is lowered into the hole. Make sure that all threaded connections are "hand-tight" and sealed before lowering a section into the hole. Record the number of pieces placed in the hole to cross-check the well depth. Do not use tools to tighten PVC joints. This will help to avoid breakage and contamination.

13. On deep wells, it may be necessary to use clamps to hold the PVC while assembling the joints. Exercise the greatest amount of caution to ensure that the well assembly is not dropped.

14. Once the well assembly has reached the bottom of the borehole, install the expansion plug in the top of the PVC to avoid dropping anything in the well. Raise the PVC assembly 0.1 to 0.3 feet off the bottom of the borehole. Using a clamp, hang and center the PVC well assembly in the center of the drill pipe.

15. Calculate the approximate volume of filter sand required to fill the annular space between the 4 inch PVC and the 8 to 12 inch HSA borehole.

16. Carefully pour a volume of sand equivalent to 1 to 2 feet of borehole annular space into the hole. Allow it to settle. (On deeper wells with greater than 50 feet of water present, the time necessary for the sand to settle may exceed 15 minutes.)

17. Slowly raise the PVC well assembly 0.1 to 0.3 ft to the required depth to provide a sand cushion at the well point. NEVER PUSH DOWN ON THE WELL ASSEMBLY.

18. Slowly add filter sand in 1 to 3 foot increments while slowly raising and removing the augers or casing. Monitor the sand level to ensure that clean filter sand is always inside the augers or the casing and to confirm the sand has not bridged. To avoid bridging of the sand pack on deeper wells it may be necessary to tremie the sand into place, using clean potable water, recording the amount of water used on the well completion form. Be careful not to pull the well up or let it drop while pulling the augers or casing.

19. Following the addition of the sand, the PVC well assembly will be raised an additional 0.1 to 0.5 ft to provide a sand cushion at the well point. Repeat step 18 until the filter sand is 2 feet or 20% of the screen length (whichever is greater) above the top of the screen. The filter sand should be six inches below the bottom of the screen length. The sand thickness above the screen may have to be reduced to less than 1.0 foot on near surface wells to allow proper surface completions. If possible, install a 1 to 2 foot layer of finer sand on top of the filter sand (total sand thickness above the screen should not exceed 6 feet). Confirm any modifications with the Site Manager before proceeding.

20. A finer grained sand pack material (100 percent passing the No. 30 sieve and less than two percent passing the No. 200 sieve) six inches thick must be placed at the top of the sand pack between the sand and the bentonite seal. The fine sand will serve as a barrier between the filter sand pack and the bentonite seal to prevent infiltration of the bentonite into the sand pack around the well screen.

21. Add bentonite chips to create the seal above the sandpack. Incrementally add medium sized bentonite chips (e.g., Enviroplug Brand) to the well. Repeatedly monitor the level of the top of the chips to avoid bridging of the seal between the PVC and drill pipe. The final bentonite seal should be at least 3 feet thick on shallow wells and up to 5 feet thick on deeper wells. Modifications recommended and approved by the field team leader may be necessary for near surface wells. Add

15 gallons of potable water to the borehole if the bentonite seal has been placed above the water table.

22. A 6 to 12 inch fine grained sand pack must be placed above the bentonite seal to minimize grout infiltration.

23. Pull casing or augers up to within a foot of the top of the bentonite seal fine sand (#00) pack. Allow approximately 1 hour for the bentonite chips to hydrate or the bentonite slurry to settle. During this time, prepare for grouting the hole.

24. Grout the annular space around the riser, above the bentonite seal fine sand (#00) pack, to a final level that is 3 to 5 feet below the ground surface using 3% by weight bentonite to cement. The grout mixture will consist of bentonite powder and water and will be an New Jersey Depart of Environmental Protection-approved grout. This mixture must be thoroughly mixed to minimize the possibility that the bentonite will lump. All grout seals installed below the water table must be tremied into place, with the tremie tube placed 2 to 5 feet above the top of the bentonite seal fine sand (#00) pack. As the grout is pumped in, the tremie pipe and augers or casing are withdrawn. Grouting will be done in one continuous operation, from the top of fine sand layer to the depth at which the cement collar is to be placed (about 3-5 feet below grade). Installed grout seals will be allowed to settle and set-up for 24 hours prior to being inspected. Additional grout will be added to bring the grout level to a final height between 2 to 3 feet below the ground surface for surface well completion. Record all details of the well completion activities on the proper attached Well Completion form.

25. Complete the concrete surface collar and surface completion two to seven days after installing the well.

26. Prior to well development, at least 48 hours will have elapsed after the well is grouted. This allows the grout to harden. The well will be developed at least seven days before groundwater monitoring activities or groundwater sampling to allow the groundwater to stabilize.

27. Spoils associated with grouting operations will be handled as a waste stream.

16.3.5.2 Bedrock Groundwater Monitoring Wells

Bedrock well installation will be identical to the unconsolidated well installation with the exception of the bedrock coring procedures and installation of a steel casing across the bedrock/overburden boundary.

After initial drill refusal at the top of bedrock, the hole will be drilled or reamed 3 to 4 feet into competent bedrock to confirm the bedrock surface and allow for the installation of the outer steel casing

into the competent bedrock. Following the initial coring into bedrock, approximately 2 feet of bentonite chips will be added to the bottom of the borehole and allowed to hydrate for 15 minutes. The steam-cleaned steel casing will be advanced to 2 feet above the bentonite seal, and grout will be tremied into the hole until undiluted grout flows from the top of the hole. The casing will be pushed into the bentonite seal. If the grout level drops during this operation, more will be added to the hole until the level stabilizes 3 feet below the ground surface.

The grouted casing will be allowed to set for a period of 48 hours prior to the initiation of coring operations, after which the boring will be advanced to a maximum depth of 20 feet below the steel casing using an HQ-size core (2.5 inches diameter) and core barrel. During coring, a potable analyte-free water will be pumped into the borehole to serve as a lubricant and to remove the fine rock flour and shale chips from the hole. The water will be recirculated into the hole after passing through a steel bath with several baffles to contain most of the rock flour and shale chips, preventing them from being reintroduced into the borehole. A description of the rock core will be recorded on the Core Boring Report according to the procedures outlined in Section 16.3.1.2, and the well completion will be detailed on the Bedrock Monitoring Well Completion Report & Installation Detail form. Both forms are contained in Appendix C.

16.3.6 Groundwater Monitoring Well Development

All installed groundwater monitoring wells require development prior to sampling. Groundwater monitoring well development will be performed to remove sediment from inside the well casing and to flush fine materials from the portion of the formation adjacent to the screen. Groundwater monitoring wells should be developed at least seven days before groundwater monitoring activities or groundwater sampling to allow the groundwater to stabilize.

16.3.6.1 Equipment

- Submersible pump, hand pump, staged submersible pump, peristaltic, or other suitable pump
- Bottom filling bailer
- Stopwatch or watch
- pH meter
- Specific conductivity meter
- Nephelometer (field portable turbidity meter)
- Thermometer
- Battery operated water level indicator
- Surge block
- Health and safety equipment as necessary
- Large funnel

- Well Development Report form (Appendix C)
- 55-gallon drum for soil
- decontamination equipment as described in Section 16.3.11
- Level D health and safety equipment as described in the Generic Site-Wide Health and Safety Plan (Parsons, 2005).

16.3.6.2 Field Procedures

1. Well development must not begin any sooner than 48 hours after the well is grouted. All data and calculations must be recorded on the attached Well Development Report form (Appendix C). Development records will include:

    - Groundwater monitoring well number;
    - Date and time of development;
    - Development method;
    - Predevelopment water level and well depth;
    - Volume of water produced;
    - Description of water produced; and
    - Post development water level and well depth.

2. Measure the groundwater elevation and well depth. Compare data to original (i.e., installed) well depth.

3. Calculate the standing water volume in the well as described on the Well Development Report form. Take into account the water standing in the riser pipe and screen as well as the water contained in the sand-pack surrounding the screen, assuming a 30 percent (%) porosity for the sand-pack.

4. Following the groundwater elevation measurement and calculations, determine the percentage of the screen covered with silt in the well by measuring the depth to the top of the silt in the well, if any is present. Determine the thickness of silt above the bottom of the screen, if present, and calculate the percentage. If the percentage is greater than 10%, remove the silt at the start of purging by lowering the intake to the bottom of the well. Once the silt has been removed, lift the pump intake to the top of the water column and continue purging.

5. In addition, remove all fines that may have accumulated within the well, as well as those that may have been smeared on the inside of the borehole during well drilling.

6. Remove 5 times the calculated standing water volume from the well (as well as any water lost to the formation during drilling) using a submersible, hand, staged submersible, peristaltic, or other

suitable pump as approved by the Site Manager. The pump selection will be made based on saturated thickness, depth to water, and rate of recovery. At the completion of the third, fourth, and fifth volume, measure the pH, specific conductivity, and the turbidity of the water. A non-turbid discharge (e.g., NTU less than 50) is sufficient to measure NAPL thickness, water level, etc. However, a "turbidity-free" discharge is required for wells used to measure groundwater quality. As a general rule these readings should be reproducible to $\pm$ 0.2 standard units for pH, 10% for specific conductivity, and $\pm$ 10 NTUs for turbidity, when the well development is complete. However, this is not a requirement.

7. If consecutive water quality measurements do not agree to the limits defined in Step 5, additional standing water volumes must be removed until the discharge meets the "turbid-free" requirement.

8. If 10 standing volumes of well water have been removed and the above criteria have not been met, compare the amount of water removed to the amount of water lost to the formation during drilling. Development will continue until either stable water quality measurements are obtained or development has removed one well volume of water in excess of the amount of water lost to the formation during drilling. At this time the well will be declared developed. The utility of wells that do not meet the development requirements must be accessed whenever samples for chemical analysis are collected.

9. When slow recoveries hamper well development operations (i.e., well is pumped dry after the removal of less than required volumes), measure the water quality parameters on the last water removed during each separate development session. If development criteria are not met within 96 hours of beginning well development, well development will continue until more water has been removed than was lost to the formation or the well has been pumped to dryness and allowed to recover five times within a seven day period from initiating well development operations. At this time the well will be declared developed. The utility of wells that do not meet the development requirements must be accessed whenever samples for chemical analysis are collected.

10. The pumped development water will be managed and disposed in accordance with the Section 16.3.12.

16.3.7 Groundwater Monitoring Well Abandonment

Groundwater monitoring wells developed during the site investigation/remediation may be abandoned for various reasons (e.g., normal completion of site activities). All abandonment of monitor wells shall be performed in accordance with federal, state, and local laws and regulations. Details of all abandonment procedures will be fully documented by photographs, depth and volume measurements, any calculations, and pertinent notes.

16.3.7.1 Equipment

- Drilling rig capable to drilling to the appropriate depth for the well
- Field monitoring and screening instrumentation
- Mud-pump
- Decontamination equipment.
- Spoils handling equipment.
- Grouting supplies (powdered bentonite, Portland cement, and water).
- Tremie pipe
- 55-gallon drum for soil
- Decontamination equipment as described in Section 16.3.11 and
- Level D health and safety equipment as described in the Generic Site-Wide Health and Safety Plan (Parsons, 2005).

16.3.7.2 Field Procedures

The procedures for the abandonment of boreholes are as follows:

1. The well should be cleared of all obstructions prior to abandonment. Obstructions such as pumps, pipes, wiring, and air lines must be pulled. An attempt should be made to pull the casing when it will not jeopardize the integrity of the borehole. Before the casing is pulled, the well should be grouted to near the bottom of the casing. This will provide a seal if the well collapses after the casing is pulled.

2. Prepare a sufficient quantity of an appropriate grout mixture to fill the hole to within 4 feet of surface grade. If more or less grout mixture than this is required, maintain the same material ratios for all additional material. The grout mixture shall consist of Portland cement (ASTM C 150-86) and water in the proportion of not more than 7.0 to 8.0 gallons of clean water per bag of cement [1 cubic foot or 94 pounds]. Additionally, 3 percent by weight of bentonite powder will be added to help reduce shrinkage of the grout mixture. The grout will be allowed to set for a minimum of 48 hours. Potable water must be used when mixing grouting materials. The amount of water used will be recorded in the field notes of abandonment procedures. If slurry is used to seal the well, a mud balance and/or Marsh Funnel shall be used to ensure that the density (lbs/gal) of the abandonment mud mixture conforms to the manufacturer's specification.

3. Pump the grout mixture into the borehole through a tremie pipe in one continuous operation, from the bottom to the top of the borehole, while removing all drilling equipment (augers, casing, etc.) from the borehole. The tremie/grout pipe may be slowly raised as the grout is being placed but the

discharge end of the pipe shall remain submerged in the grout at all times until grouting is complete.

4. When grouting a borehole, the grout must extent up to the ground surface. Then, allow the grout to settle and regrout as necessary.

5. All abandoned monitor wells shall be checked 24 to 48 hours after mud/solid bentonite emplacement to determine whether curing is occurring properly. More specific curing requirements or quality assurance checks may be recommended by the manufacturer and shall be followed. Additionally, if significant settling has occurred, a sufficient amount of mud/solid bentonite shall be added to attain the initial level. These slurry/solid bentonite curing checks and any addition of mud/solid bentonite shall be recorded in the field logs.

6. The driller must maintain an accurate written log of all materials encountered, record details for each boring, and record the depth of each water bearing zone. This information must be submitted to the Parsons project manager.

7. Manage the residual soil and grout as directed by Section 16.3.12.

8. Mark the boring location with a stake or flag so the location can be surveyed.

9. Decontaminate the equipment.

16.3.8 Aquifer Slug Tests

A slug test is a single-well hydraulic test used to determine the hydraulic conductivity of an aquifer in the immediate vicinity of the screened interval of the tested well. Slug tests can be used for both confined and unconfined aquifers that have a transmissivity of less than 7,000 square feet per day. Slug testing can be performed using either a rising head or a falling head test. This section describes the slug test that uses both methods in sequence.

Slug tests are used to test properties of aquifers with rocks or unconsolidated deposits of low to moderate hydraulic conductivity. Testing of several wells is necessary to characterize an aquifer because slug tests only measure aquifer properties immediately adjacent to the borehole or well. The water level shall be static before the test begins. That is, it must not be recovering or receding as a result of sampling, development, pumping of nearby wells, or related activities. The test shall be performed using a slug or by withdrawing water from the well. No fluid shall be put into the well.

All valid water-level or drawdown versus time data resulting from these tests should be appended to the draft and final reports describing the analysis of these tests. These field data should be provided in ASCII electronic format. Additionally, these field data and the calculated hydraulic conductivity values

will be included in the report and submitted to the Army. A field slug test report form is attached in Appendix C.

When designing a slug test, the geologist should identify the following parameters: (1) volume of the slug, (2) diameter of the well, (3) depth and length of the screened interval, (4) method and frequency of water level measurements, (5) barometric pressure, and (6) the method used to analyze the data.

16.3.8.1 Definitions

Hydraulic Conductivity (K). A quantitative measure of the ability of porous material to transmit water; defined as the volume of water that will flow through a unit cross-sectional area of porous or fractured material per unit time under a unit hydraulic gradient.

Transmissivity (T). A quantitative measure of the ability of a given thickness of an aquifer to transmit water. It is the product of the hydraulic conductivity and the saturated thickness of the water-bearing zone.

Rising Head Test. A test used in an individual well within the saturated zone to estimate the hydraulic conductivity of the surrounding formation adjacent to the screened interval by lowering the water level in the well and measuring the rate of recovery of the water level. The water level may be lowered by removing a quantity of water or a submerged solid slug from the well. The well screen may be fully or partially saturated during the test.

Falling Head Test. A test used in an individual well to estimate the hydraulic conductivity of the surrounding formation adjacent to the screened interval by raising the water level in the well by insertion of a solid slug or quantity of water, and then measuring the rate of drop in the water level. If the static water level is below the top of the screen or open section of the well, a falling-head test should not be performed.

16.3.8.2 Equipment and Materials

The following equipment will be used to conduct a slug test:

- Teflon®, PVC, or metal slugs;
- Nylon or polypropylene rope;
- Electric water-level indicator;
- Pressure transducer/sensor (10 psi recommended);
- Field logbook/forms; and
- Automatic data recording instrument (e.g., Hermit Environmental Data Logger®, In-Situ, Inc. Model SE3000, or equivalent).

16.3.8.3 Test Procedures

Hydraulic testing will be completed on wells that have been properly developed and in which water levels have stabilized. During the slug test, the water level change should be influenced only by the introduction (or removal) of the slug volume. Other factors, such as inadequate well development or extended pumping, may lead to inaccurate results. The Parsons field team will determine when static equilibrium has been reached in the well. The pressure transducer, slugs, and any other downhole equipment will be decontaminated prior to and immediately after the performance of each slug test using the procedures described in Section 16.3.11.

One falling and one rising head test will be performed at each selected monitoring location. The following steps describe the falling and rising head slug test procedure:

1. Decontaminate all downhole equipment prior to initiating the test.

2. Open the well. Where wells are equipped with water-tight caps, the well should be unsealed at least 24 hours prior to testing to allow the water level to stabilize. The protective casing will remain locked during this time to prevent vandalism.

3. Prepare the aquifer slug test report form (attached in Appendix C) with entries including:

    a. Well number, project number, and project name,
    b. Aquifer testing team,
    c. Climatic data,
    d. Measuring equipment being used, and
    e. Date.

4. Measure the static water level in the well to the nearest 0.01 foot.

5. Lower the decontaminated pressure transducer into the well and allow the displaced water to return to its static level. This can be determined by periodic water-level measurements until the static water level in the well is within 0.01 foot of the original static water level. At least one foot should be allowed between the bottom of the well and the transducer, and there must be enough space between the transducer and the water table to submerge the slug (verify length of slug needed prior to test).

6. Prepare the data logger for the <u>falling head</u> test in accordance with the user's manual. Set the data logger to record in logarithmic mode and reference the transducer to zero prior to the test. Follow the user's manual for proper operation of the data logger.

7. Turn on the data logger, initiate data recording, and quickly lower the slug into the well using clean nylon rope so that the top of the slug is just below the static water level previously measured in the well, being careful not to disturb the pressure transducer. The hollow stainless steel slug should contain machined ends onto which stainless screw caps with o-ring gaskets fit. The slug should be filled with potable water for the test. In some instances a thinner, solid 2-foot long slug should be used for the slug test if the 5-foot slug becomes repeatedly snagged on the transducer cable at the start of the test, thereby disrupting the test results.

8. Stop data recording when the water level reaches 80 percent of the original static water level and stabilizes to 0.02 feet over a 5-minute time period. During the test, water levels can be monitored using the data logger display.

9. Prepare data logger for the rising head test in accordance with the user's manual. Set the data logger to record in logarithmic mode and reference the transducer to zero prior to the test

10. Initiate data recording again and quickly remove the slug from the well (make sure not to disturb the transducer cable) and continue the test until the water level in the well has stabilized. The well will be considered stabilized for termination purposes when it has recovered to within 10 percent of the original static water level.

11. Terminate data recording when the water level reaches 80 percent of the original static water level and stabilizes to 0.02 feet over a 5-minute time period.

12. Remove the transducer from the well and decontaminate.

16.3.8.4 Slug Test Data Analysis

Data obtained during slug testing will be analyzed using the method of Bouwer and Rice (1976) and Bouwer (1989) for unconfined conditions.

16.3.8.5 Other Aquifer Test Methods

Other aquifer test methods could be used to estimate the aquifer hydraulic parameters (e.g., transmissivity and storativity) and if needed, will be specified in the SS-WP. Below are some of the test methods that could be used to estimate aquifer hydraulic parameters.

- ASTM D-4630-96(2002), Standard Test Method for Determining Transmissivity and Storage Coefficient of Low-Permeability Rocks by In Situ Measurements Using the Constant Head Injection Test

- ASTM D4631-95(2000), Standard Test Method for Determining Transmissivity and Storativity of Low Permeability Rocks by In Situ Measurements Using Pressure Pulse Technique

- ASTM D2434-68(2000), Standard Test Method for Permeability of Granular Soils (Constant Head)

16.3.9 Test Pit/Trench Excavation

The primary objective of test pitting is to provide a means for the visual evaluation of subsurface soils and the collection of soil samples or to investigate anomalies discovered during the geophysical surveys. Test pits and trenches shall be excavated by hand or by power equipment to permit detailed observation of in-situ materials. Hand digging around specific materials encountered may be necessary to prevent puncture or damage of the objects. Sufficient space should be maintained between trenches/pits for the placement of soil stockpiled for cover as well as to allow access and free movement by support vehicles and operating equipment. The protocol presented in this section is consistent with the guidance document developed by USEPA (1987). Safe work practices for excavation and test pitting, which can be found in the Generic Site-Wide Health and Safety Plan (Parsons, 2005), should be used for any test pit/trench excavation activities.

16.3.9.1 Equipment

- Excavator
- Shovels and other hand tools
- Tape measure
- Folding ruler
- Test Pit Record form (Appendix C)
- FID or PID
- Field book
- Decontamination equipment as described in Section 16.3.11.
- Level D health and safety equipment as described in the Generic Site-Wide Health and Safety Plan (Parsons, 2005).
- Camera

16.3.9.2 Field Procedures

Test pits and trenches will be excavated by backhoe to permit detailed observation of in-situ subsurface soils. Hand digging around specific materials or utilities encountered may be necessary to prevent puncture or damage of objects. Test pits are typically 3 to 7 feet wide and 8 to 15 feet deep; test trenches are typically 3 to 6 feet wide and may be extended for any length required to reveal conditions along a specific profile line. However, actual excavation widths and depths are dependent on the

backhoe size, depth to groundwater, and soil conditions encountered and will be specified in the SS-WP.

1. Conduct pre-excavation check as described in Section 16.3.2.

2. Inspect all excavating equipment.

3. Decontaminate all excavating equipment as per Section 16.3.11 prior to starting the work. Inspect all equipment to assure that residual oils, asphalt, grease, grout, soil, etc. has been removed.

4. Mark the location of the proposed test pits and trenches in the field.

5. While excavating in parking areas or improved grassy areas, excavated materials will be stockpiled on polyethylene sheets beside the test pit. While excavating in landfill areas with unimproved dirt surfaces, only obviously contaminated materials, different from surface material, will be placed on plastic, where practical. The staging area should include run-off containment features. Keep the top 6 to 12 inches of soil separate from the deeper soil so that it can be used as cover material when the test pit is backfilled. The size and depth of the test pit or trench will be described in the SS-WP.

6. When appropriate, air sampling will be performed during test pitting to support two broad-based directives: the protection of workers and the protection of public safety. Air sampling shall be performed using a Photoionization Detector with an 11.7 mV lamp to monitor for volatile organic compounds in the air. It will be used to monitor air in the breathing space of workers during test pit activities. The procedures for any necessary air monitoring will be specified in the SS-WP or site-specific Health and Safety Plan.

7. The field team will keep detailed records on the Test Pit Record form (attached in Appendix C) including:

    a. Soil descriptions and stratigraphic changes;

    b. Relative soil moisture; depth to groundwater (if encountered);

    c. Visible signs of staining (natural or otherwise);

    d. Level of difficult of excavation

    e. Results, type, and time of monitoring measurements;

    f. Sampling locations, depths, and time;

g. Time of excavation;

h. Reason for terminating excavation; and

i. Type of excavator.

8. Significant features exposed by the test pit and trench will be photographed, if possible, with a scale included in the photographs to indicate dimension. The photographs of test pits will be marked to include site number, test pit number, depth, description of feature, and date of photograph. Where photographic records are collected, a detailed log will be maintained noting location, feature, time, and date.

9. Trained personnel adhering to appropriate safety and health standards shall collect samples from the test pit as directed by the field team leader. The samples will be obtained in accordance with split spoon sampling SOPs presented in Section 16.4.2.

10. **No personnel will be allowed to enter the excavation once the excavation is more than 2 feet deep**, unless proper safety precautions have been taken, such as wall slopes or trench boxes, in accordance with OSHA standards.

11. Any excavated containers filled with liquid or solid substances will be overpacked, tested, and appropriately disposed in accordance with SOPs presented in Section 16.3.12.

12. If the pit is not to be closed immediately after the required samples have been obtained, the excavation will be barricaded to prevent accidental entry by personnel working on the site.

The following describes the procedures for test pit and trench termination/completion:

1. Each test pit and trench will be backfilled with the excavated material. The material will be placed in lifts of 1 to 2 feet. Each lift will be compacted with the bucket of the excavator. The segregated surface soil will be backfilled last. The ground surface conditions should be returned to the existing conditions after the completion. Previously paved surfaces removed for test pit excavation will be graded and patched with bituminous pavement matching the thickness of the original pavement to form a level surface with the adjacent pavement.

2. Upon closure of the excavation, mark the test trench or pit with a stake or flagging, labeled with the test pit or trench number, so that its location can be surveyed.

3. Decontaminate the backhoe bucket and arm upon completion of excavation activities in accordance with Section 16.3.11 before new excavations begin.

4. All wastes generated in association with test pit or trench operations will be managed as per SOP presented in Section 16.3.12.

16.3.10 Sample Location Survey

This section outlines the location survey activities to be conducted during the field activities. The surveying data will be used to develop the technical reports for the site and to support the field effort.

16.3.10.1 Sample Location Survey

The locations and elevations of monitoring wells, soil borings, surface soil samples, sediment samples and surface water samples will be surveyed by a surveyor registered in the State of New York. The elevation of the ground surface adjacent to each surveyed point and measurement datum will be measured relative to an existing benchmark location referencing the Base grid system. Survey of the new wells will take place as follows:

- Horizontal locations for monitoring wells, soil borings, surface soil, sediment and surface water sample locations will be measured relative to Northing and Easting in State Planar Coordinates, North American Datum of 1983 (NAD 1983), accuracy ± 0.1 feet.

- The elevation of the ground surface adjacent to each monitoring well will be measured relative to North American Vertical Datum of 1988 (NAVD 1988), accuracy ± 0.1 feet at stake or pin in collar.

- The elevation of the top of the well protective casing and top in the well casing will be measured relative to NAVD 1988, accuracy ± 0.1.

- Monitoring wells will have three elevations with varying levels of accuracy; the first for the top of well's PVC inner casing at a notch placed by the surveyor, a second for the top of the well's protective outer casing at the crown of the cap, and the last for the elevation at a pin placed in the collar of the well at the ground.

All monitoring wells shall be resurveyed at a minimum every five years, with the approval of the Army.

Other potential site surveys include preliminary alignment survey, preconstruction alignment survey; and post construction as-built survey. These surveys will also be conducted by a surveyor registered in the State of New York. Requirements for other site-specific surveys, if warranted, will be covered in the SS-WP.

16.3.10.2 Survey Grids

The geophysical investigation will incorporate two distinct methods of survey and mapping of anomaly locations. The first method will involve the establishment of a survey grid with size specified in the SS-WP on a planimetric map prior to entering the field. The grid will first be established on a map and submitted to Parsons and USACE for approval. Once approved, the associated grid will then be surveyed in to its proper location once the field investigation begins.

Land survey activities include field survey and mapping of each grid using grid coordinates provided by Parsons. The corners of each grid shall be referenced to the New York State Plane Grid System based on the North American Datum of 1983 (NAD 1983). All grid locations will be surveyed, the coordinates recorded, and semi-permanent marker stakes will be advanced at each grid corner prior to investigation of a grid. The corners of the individual grids will be established to a post-processed accuracy of ± one foot. Grids will be oriented north-south or east-west, where possible, to enable quick tracking of grid locations and access to each grid during subsequent investigations.

Approved survey techniques will be used to place the southwest corner of each survey grid to within approximately 25 meters of their proposed locations in this Work Plan. The remaining corners of the survey grids will then be located. If the location of a grid falls in an area that would not be accessible to the geophysical survey crew (i.e. a ravine), or is in an area with significant cultural interference (such as irrigation piping), that grid will be relocated up to 50 meters from the originally selected location.

Grid corners may be laid out using a combination of surveyors' equipment, differential GPS equipment, and trigonometry. At a minimum, the southwest corner of each grid will be established using GPS or surveying methods. The horizontal accuracy of the geophysical surveys and the ability of the OE characterization/investigation team to reacquire anomalies will be greatly dependent upon the placement of the grid corners. The angle between the survey grid boundaries must be as close to 90 degrees as possible, and will periodically be verified for "squareness" by the survey crews. A grid found to be out of square by more than 1 foot (measured diagonally from grid corner to grid corner) will be resurveyed. EM-61 data collected from a grid that is found to be out of square will either be corrected (if possible) or the grid will be adjusted and resurveyed with the EM-61.

16.3.11 Equipment Decontamination

Sample collection devices will be decontaminated prior to each use. All potentially hazardous rinse liquids and materials will be containerized and properly disposed, in accordance with Section 16.3.12. Decontamination methods will be modified if necessary, based on the SS-WP. Equipment decontamination will be conducted in a clean area free of dust. Precautions will be taken to minimize any impact to the surrounding area that might result from decontamination operations, and any

deviations from these procedures will be documented in the field notebook and on the appropriate sampling record.

Laboratory-supplied sample containers will be cleaned and sealed by the laboratory. The type of container provided and the method of container decontamination will be documented in the laboratory's permanent record of the sampling event.

Decontamination procedures for sample collection equipment, submersible pump and water level indicator, above-ground pump, and drill rigs are provided below. Unless otherwise specified, Liqui-Nox (or a non-phosphate equivalent) will be used as the cleaning reagent. Alconox (or equivalent) can be substituted if the sampling equipment will not be used to collect phosphorus or phosphorus-containing compounds. Unless otherwise specified, ambient temperature water may be substituted in the hot water bath or rinses. Unless otherwise specified, pesticide grade solvent (isopropanol) should be used for decontamination. This grade of alcohol must be purchased from a laboratory supply vendor. Rubbing alcohol or other commonly available sources of isopropanol **are not acceptable**.

16.3.11.1 Decontamination of Sample Collection Equipment

Sample collection equipment (e.g., bailers, stainless steel scoops/spoons, trowels, coring bits, and hand auger bucket) used to collect groundwater, surface soil, subsurface soils, surface water, or sediment will be decontaminated by the following process:

1. Wash equipment with hot tap/potable water.

2. Soak equipment in a hot detergent (Alconox or Liquinox) solution. Use Liquinox if the sampling equipment will be used to collect phosphorus or phosphorus-containing compounds. A scrub brush will be used to remove dirt and surface film.

3. Rinse thoroughly with tap water.

4. For Teflon®, stainless steel, and glass sampling equipment:

    - If samples for trace metals or inorganic analytes (other than nitrogen components such as nitrate and nitrite) will be collected with the equipment and the equipment **is not** stainless steel, thoroughly rinse (wet all surfaces) with 10% reagent grade nitric acid. If sampling for ultra-trace levels of metals, use an ultra-pure grade acid. Use reagent grade 10% hydrochloric acid when nitrogen components are to be sampled.

    - If samples for organics will be collected, rinse with pesticide grade isopropanol.

5. For plastic sampling equipment, thoroughly rinse (wet all surfaces) with 10% reagent grade nitric acid (for analytes other than nitrogen components) or reagent grade 10% hydrochloric acid (for nitrogen component samples). Check manufacturer's instruction for cleaning restrictions and/or recommendations.

6. Rinse thoroughly with deionized, organic-free, reagent grade water.

7. Remove excess water and allow equipment to air dry.

8. Wrap equipment in aluminum foil, shiny side out.

9. Rinse water and detergent water will be replaced with new solutions daily, when visibly impacted by residuals, or between sampling areas or changes in operations.

16.3.11.2 Decontamination of Submersible Water Level Indicator

Submersible water level indicators will be decontaminated with the following procedure:

1. Wash outside of water level indicator and hoses/lines with laboratory-grade detergent (Alconox or Liquinox) and water.

2. Rinse outside of water level indicator and hoses/lines with potable water.

3. Rinse outside of water level indicator and hoses/lines with deionized, organic-free, reagent grade water.

4. Remove excess water.

5. Wrap water level indicator in plastic.

16.3.11.3 Sample Tubing Decontamination

Sample tubing will be decontaminated by the procedures listed below prior to use and following sampling of each well. The SOP was modified from the SOPs developed by Florida DEP (2004).

1. Check tubing for discoloration and elasticity. Remove discolored tubing from use until it can be cleaned. If the discoloration cannot be removed, discard the tubing. Discard any tubing that has lost its elasticity.

2. Transport all tubing to the filed in precut, **precleaned** sections.

3. Teflon®, Polyethylene and Polypropylene Tubing

It is recommended that **used tubing not to be used for sampling**. If warranted, used tubing has to be cleaned in laboratory. Field cleaning is not recommended. An SOP for used tubing cleaning will be developed and presented in the SS-WP if warranted. Follow the following procedures to clean new tubing unless the manufacturer/supplier provides certification that the tubing is clean.

3.1 Teflon®

3.1.1 Rinse outside of tubing with pesticide-grade isopropanol

3.1.2 Flush inside of tubing with pesticide-grade isopropanol.

3.1.3 Dry overnight in drying oven or equivalent (zero air, nitrogen, etc.)

3.2 Polyethylene and Polypropylene

3.2.1 Clean the exterior and interior of the tubing by soaking in hot (or ambient temperature if not practical) Liqui-Nox or Alconox detergent solutions. Do not use Alconox for sampling for phosphorus or phosphorus-containing compounds.

3.2.2 Thoroughly rinse the exterior and interior of the tubing with tap water, followed by deionized, organic-free, reagent grade water.

4. Flexible Tubing used in Pump Heads of Automatic Samplers and Other Peristic Pumps

Replace tubing after each sampling point if samples are collected through the tubing. Unless the pump is deployed to collect samples from the same location over a long period of time, remove and wash the tubing after each sampling event.

4.1 Flush tubing with hot tap water then detergent solution.

4.2 Rinse thoroughly with hot tap water.

4.3 Rinse thoroughly with deionized, organic-free, reagent grade water.

4.4 If used to collect metal samples, flush the tubing with a 10% reagent grade nitric acid, followed by thorough rinsing with analyte-free water. If used to collect both metals and nitrogen components use 10% reagent grade hydrochloric acid.

4.5 Install tubing in peristallic pump or automatic sampler.

4.6 Cap both ends with aluminum foil or equivalent.

5. Stainless Steel Tubing

5.1 Using appropriate detergent solution to scrub the interior and exterior surfaces.

5.2 Rinse with hot tap water.

5.3 Rinse with deionized, organic-free, reagent grade water.

5.4 If volatile or extractable organics are to be sampled, rinse all surfaces with pesticide grade isopropanol. Use enough solvent to wet all surfaces with free flowing solvent.

5.5 Allow to air dry or thoroughly rinse with deionized, organic-free, reagent grade water.

6. Glass Tubing

6.1 Use new glass tubing.

6.2. If volatile or extractable organics are to be sampled, rinse with detergent grade isopropanol.

6.3 Air dry for at least 24 hours.

6.4 Wrap in aluminum foil or untreated butcher paper to prevent contamination during storage.

6.5 Discard tubing after use.

7. Miscellaneous Non-Inert Tubing Types (Tygon®, Rubber, PVC, Etc.)

7.1. New Tubing

7.1.1 As a general rule, new tubing may be used without preliminary cleaning.

7.1.2 Protect new tubing from potential environmental contamination by wrapping in aluminum foil and sealing in untreated plastic bags or keep in the original sealed packaging unit use.

7.1.3 If new tubing is to be used to collect samples, thoroughly rinse the tubing with sample water (i.e., pump sample water through the tubing) before collecting samples.

7.2. Reused Tubing

7.2.1. Flush tubing with appropriate detergent solution (Liqui-Nox, Alconox, or equivalent).

7.2.2 Rinse exterior and interior thoroughly with hot tap water.

7.2.3 Rinse exterior and interior thoroughly with deionized, organic-free, reagent grade water.

7.2.4. If used to collect metals and nitrogen-containing compounds, flush the tubing with 10% reagent grade nitric acid, followed by a thorough rinse with deionized, organic-free, reagent grade water.

7.2.5 If used to collect metals and nitrogen-containing compounds, use the 10% reagent grade hydrochloric acid rinse, or thoroughly rinse with hydrochloric acid after a nitric acid rinse.

7.2.6. Cap ends in aluminum soil and store in clean, untreated plastic bags to prevent contamination during storage and transport.

16.3.11.4 Decontamination of Submersible Pumps

Submersible pump (including support cable and electrical wires which are in contact with the sample) will be decontaminated by one of the procedures listed below prior to use and following sampling of each well. The SOP was modified from the SOPs developed by Florida DEP (2004).

Procedure 1 – Pumps Used for Purging and Sampling Metals and/or Volatile and Extractable Organics

1. Clean pump exterior following steps presented in Section 16.3.11.1. Omit the solvent rinse if the pump body is constructed of plastic (e.g., ABS, PVC, etc.)

2. If used only for purging, thoroughly flush the pump with water before purging the next well, followed by steps 4 through 6 presented below.

3. If used for purging and sampling, completely disassemble the pump (if practical) and decontaminate between each well. When used for purging and sampling and the pump cannot be (practicably) disassembled, then clean the internal cavity/mechanism by pumping five gallons of tap/potable water and laboratory-grade detergent (Alconox or Liquinox), followed by five gallons of tap water, and finally, five gallons of deionized, organic-free, reagent grade water.

4. Clean sample tubing as presented in Section 16.3.11.3.

5. Remove excess water and allow equipment to dry.

6. Wrap pump hose in plastic, and pump in aluminum foil.

* Please note that when decontaminating centrifugal pumps manufactured by GRUNDFOS, the motor coolant chamber contains water and potential contaminants from prior usage. Therefore, to avoid cross contamination, the coolant fluid must be removed and replaced. See manufacturer's installation and operating instructions for further details.

Procedure 2 – Pumps Used for Purging and Sampling all Analytes except Metals and Volatile and Extractable Organics

1. Scrub the exterior of the pump with appropriate metal-free, phosphate-free, or ammonia-free detergent solution (e.g., Liqui-Nox solution).

2. Rinse the exterior with tap water and deionized, organic-free, reagent grade water.

3. Rinse the interior of the pump and tubing by pumping tap or deionized, organic-free, reagent grade water through the system using a clean bucket or drum.

4. Remove excess water and allow equipment to dry.

5. Wrap pump hose in plastic, and pump in aluminum foil.

* Please note that when decontaminating centrifugal pumps manufactured by GRUNDFOS, the motor coolant chamber contains water and potential contaminants from prior usage. Therefore, to avoid cross contamination, the coolant fluid must be removed and replaced. See manufacturer's installation and operating instructions for further details.

16.3.11.5 Decontamination of Above-Ground Pumps

Above-ground pump will be decontaminated by the procedures listed below prior to use and following sampling of each well. The SOP was modified from the SOPs developed by Florida DEP (2004).

1. For pumps used only for purging, the exterior of the pump must be free of oil and grease, followed by the steps 3 described as below.

2. For pumps used for sampling, clean the exterior of the pump with a detergent solution followed by a tap water rinse. Use clean cloths or unbleached paper towels that have been moistened with the appropriate solution to wipe down the pump.

3. Clean the tubing that contacts the formation water according to the appropriate protocol specified in Section 16.3.11.3.

* Please note that when decontaminating centrifugal pumps manufactured by GRUNDFOS, the motor coolant chamber contains water and potential contaminants from prior usage. Therefore, to avoid cross contamination, the coolant fluid must be removed and replaced. See manufacturer's installation and operating instructions for further details.

16.3.11.6 Decontamination of the Drilling Rig and Heavy Equipment

The drilling rig and other heavy equipment will be decontaminated with the following procedure:

1. Any portion of the drilling rig that will be over the borehole, including hollow stem augers, will be cleaned with pressurized hot water.

2. Down-hole tools such as augers will be brushed cleaned using soap and tap water if pressure cleaning does not remove particulate matter.

3. Split spoons, used to collect soil samples, will be cleaned as described in Section 16.3.11.

4. Cleaned down-hole equipment such as augers, will be placed on clean tarps, racks, or sawhorses to dry.

5. After drilling equipment has been allowed to dry, it will be covered with clean, unused plastic.

16.3.11.7 Decontamination of Temporary Well Casing and Screen

The well points, screens and associated riser pipe must be decontaminated prior to installation using the following procedure:

1. Remove all adherent soil material with a stiff wire brush,

2. Wash well point and associated rise pipe and couplings with a laboratory glassware detergent,

3. Rinse with potable water and/or steam clean, and

4. Rinse the interior of well point and riser with distilled and de-ionized ASTM Type II water.

Note: for proper decontamination stronger cleaner agents are recommended with the tool has been exposed to heavy contamination. This can be performed prior to Step 2, above.

16.3.11.8 Decontamination of Filtration Equipment

Filtration equipment will be decontaminated by one of the procedures listed below prior to use. The SOP was modified from the SOPs developed by Florida DEP (2004).

Procedure 1 – Dissolved Constituents Using In-line, Molded and Disposable Filter Units

1. Peristaltic Pump

   1.1. Clean the exterior of the pump with a detergent solution followed by a tap water rinse. Use clean cloths or unbleached paper towels that have been moistened with the appropriate solution to wipe down the pump.

   1.2 Clean the tubing that contacts the formation water according to the appropriate protocol specified in Section 16.3.11.3.

   1.3. Clean the pump head tubing following step 4 presented in Section 16.3.11.3.

   1.4. If Teflon® tubing is used, clean following the step 3 in Section 16.3.11.3.

   1.5. Clean other tubing types such as polyethylene according to the step 7 in Section 16.3.11.3.

2. Other Equipment Types (e.g., pressurized Teflon® bailer)

   2.1. Follow the appropriate cleaning regimen specified in Section 16.3.11.1 (Decontamination of Sample Collection Equipment) for other types of equipment that utilize in-line, molded and disposable filters.

Procedure 2 – Dissolved Constituents Using Non-disposable Filtration Units (e.g., Syringes, "Tripod Assembly")

1. Stainless Steel or Glass Units

   1.1. Follow the appropriate cleaning regimen specified in Section 16.3.11.1 (Decontamination of Sample Collection Equipment), assembling and applying pressure to the apparatus after each rinse step (water and acid) to drive rinsing solution through the porous filter holder in the bottom of the apparatus.

   1.2. Remove and clean any transfer tubing according to the appropriate cleaning procedures specified in Section 16.3.11.3.

1.3. Assemble the unit and cap both the pressure inlet and sample discharge lines (or whole unit if a syringe) with aluminum foil to prevent contamination during storage.

1.4. If the unit will not be used to filter volatile or extractable organics, seal the unit in an untreated plastic bag to prevent contamination.

2. Reusable In-Line Filter Holders

2.1. Clean using the appropriate cleaning regimen specified in Section 16.3.11.1 (Decontamination of Sample Collection Equipment, assembling and applying pressure to the apparatus after each rinse step (water and acid) to drive rinsing solution through the porous filter holder in the bottom of the apparatus.

2.2. Assemble the unit and wrap with aluminum foil to prevent contamination during storage.

2.3. If the unit will not be used to filter volatile or extractable organics, seal the unit in an untreated plastic bag to prevent contamination.

3. Filters

3.1. Do not clean filters. Use a new filter for each sample.

3.2 Flush the filter with 30-50 mL of deionized, organic-free, reagent grade water, or an inert gas (nitrogen) to remove atmospheric oxygen; or insert the filter on the high pressure side (i.e., on the delivery side) of the pump. Hold the filter upright with the inlet and outlet vertical. Pump water from the aquifer through the filter until all atmospheric oxygen has been removed.

16.3.11.9 Decontamination of Permanent Monitoring Well Casing and Screen

Before installation, field cleaning of the well casing must consist of a manual scrubbing to remove foreign material and steam cleaning, inside and out, until all traces of oil and greases are removed. Special attention should be given to threaded joints or weld burn residues. The casing should then be handed and stored in such manner so as to prevent cross contamination prior to installation.

16.3.12 Investigation Derived Waste Disposal

This section provides the general procedures for containing, sampling, and disposing of investigation derived waste. IDW may include, but is not limited to soil, sediment, purge water, drilling water, decontamination water, excavation spoils, excavation water, sampling and decontamination equipment, and personal protective equipment (PPE). The objective is to ensure that any waste generated as a

result of field activities is disposed of in accordance with applicable local, state, and federal laws and regulations.

16.3.12.1 Containerization

Unless otherwise specified in this generic SAP or SS-WP, all IDW generated during fieldwork activities will be segregated by type and location (if warranted) and placed in sealed 55-gallon drums. At the completion of the project, any drums will be disposed appropriately. PPE and sampling equipment such as tubing will be disposed as uncontaminated refuse and the rationales are provided in Section 16.3.12.3.

Decontamination Fluids and Calibration Fluids. Decontamination fluids (including steam condensate from steam cleaning of equipment and rinse water) and calibration fluids will be collected in DOT-approved 55-gallon drums. The drums will be labeled as investigation derived wastewater and temporarily stored in a secured area to be determined prior to commencement of field activities. The drums will be stored on wooden pallets in a plastic-lined containment area or in other approved secondary containment structures pending characterization and disposal.

Drill Cuttings and Surface Soil from Well Pad Installation. Subsurface soil from drill cuttings and surface soil from well pad installation will be contained in 55-gallon drums. The soils will be segregated by drill location as is practical. The drums will be labeled as investigation derived waste soils from the corresponding boring or source area and temporarily stored in a secured area to be determined prior to commencement of field activities. The drums will be stored on wooden pallets in a plastic-lined containment area or in other approved secondary containment structures pending characterization and disposal.

Development and Purge Water. All development and purge water will be contained in 55-gallon drums. The drums will be labeled as investigation derived wastewater and temporarily stored in a secured area to be determined prior to commencement of field activities. The drums will be stored on wooden pallets in a plastic-lined containment area or in other approved secondary containment structures pending characterization and disposal.

16.3.12.2 Sampling and Evaluation

IDW will be sampled and analyzed (if necessary) in accordance with the SS-WP. Analytical results (e.g., TCLP results and waste concentration results) will be used to determine the final disposition of the waste.

The IDW strategy for drum contents classification is depicted in Figure 4. As a first step, the Toxicity Characteristic Leaching Procedure (TCLP) criteria specified in the 6 NYCRR, Part 371, Section 371.3

will be used for RCRA hazardous or non-hazardous classification**.** If TCLP data are not available, as an alternative, the "twenty times rule" described in the NYSDEC Spill Technology and Remediation Series (STARS) MEMO #1 (NYSDEC, 1992) can be used for soils. The "twenty times rule" compares the soil concentrations to twenty times the TCLP regulatory levels). This represents the soil concentration that would be classified as hazardous by exceeding the TCLP levels, assuming 100% extraction efficiency. Parsons made the conservative assumption that if one soil sample associated with the drum contents exceeded this limit then the entire drum would be characterized as RCRA hazardous waste.

Secondly, waste ignitability, corrosivity, reactivity, and toxicity will be evaluated against RCRA criteria. If these data are not available, site investigation data (e.g. detected analyte concentrations in soils, water, and drummed materials, water pH) will be used to evaluate whether the waste is *characteristic* hazardous waste (i.e., ignitability, corrosivity, reactivity, or toxicity above RCRA criteria for a characteristic hazardous waste).

IDW determined to be non-hazardous waste according to the TCLP and RCRA definition, will further be evaluated to determine if the IDW were contaminated based on soil TAGM criteria or NYSDEC groundwater standards for groundwater or purge water. This was required to evaluate compounds detected without TCLP data. If the soil result exceeded a TAGM or the water result exceeded a NYSDEC groundwater standard then the IDW was classified as contaminated. If the soil data did not exceed a TAGM value and the water results did not exceed a groundwater standard then the IDW was classified as uncontaminated.

The next step in the IDW evaluation process was to consider the threat or risk that the contaminated IDW may contribute to human health and the environment. IDW that poses an unacceptable risk or threat will then be disposed of off-site as hazardous waste. This determination involved comparison of each soil data point of the contaminated drums to ten times the TAGM value. If any soil concentration data point exceeded ten times the TAGM value then the drum contents, if disposed of on-site, is considered an unacceptable risk to human health and the environment and the drum will be disposed of off-site. Exceptions to this criteria were made if the exceedances to the ten times the TAGM value were due to non-toxic metals such as calcium, iron, manganese, potassium and sodium.

Parsons will use ten times the TAGM value as the criterion for determining whether or not the IDW poses any threat. The factor of 10 was applied due to the conservative nature of the TAGM values and the fact that this criterion has been acceptable to NYSDEC for similar SEDA projects in the past.

For the IDW waste including decontamination fluids, sampling equipment such as tubing, personal protection equipment, and purge water during the well development and sampling, the disposal evaluation involved the following steps. Under RCRA, wastes are classified as hazardous if they are listed wastes or characteristic wastes. Waste specific information, such as manifests, bills of lading, storage records or

records of waste sources must be used to document that a waste is a RCRA-listed waste; otherwise, in the absence of any other information, the waste in question cannot be considered a listed waste. Drummed cuttings, PPE, sampling tubing, or purge water generally are not listed hazardous wastes since these material produced at the Seneca sites generally do not meet any of the regulatory definitions described in 40 CFR 261, (i.e. F-, K-, P- or U- listed wastes). The only listed waste that may be generated during the investigation program at SENECA is waste that contained methanol. Methanol may be used to preserve soil/sediment samples for VOC analysis. For the Depot projects, preserved bottles will be ordered from the laboratory; therefore, unless accidentally spilled, methanol is not expected to be in any IDW waste. Wastes containing spilled methanol will be considered an F003 listed hazardous waste. An F-listed waste classification refers to non-specific hazardous waste sources that contain methanol as a component of a spent solvent mixture. In order to limit the generation of hazardous waste, methanol spilling will be reported to the project manager and the waste containing methanol should not be mixed with soils or other liquids. Additionally, during the decontamination process, washable rubber bibs will be worn to prevent contamination of disposable PPE. Overall, drummed cuttings, PPE, sampling tubing, and purge water are generally not considered hazardous waste and will be disposed of as uncontaminated refuse.

Table 22 presents the RCRA Hazardous Waste Determination Criteria and Table 23 summarizes the disposal classification process.

16.3.12.3 Disposal

IDW will be disposed appropriately based on the sampling and evaluation results. RCRA hazardous waste will be disposed of off-site by a permitted hazardous waste disposal subcontractor. Uncontaminated material will be returned to the location where it was generated. No hazardous contaminated material but with no threat to human health or the environment (e.g., soil with concentrations above TAGM but below ten times the TAGM levels) will also be returned to the location where it was generated. Uncontaminated water will be discharged to the Seneca County Sewer District No. 2 (the District) via an on-site sanitary sewer. No hazardous contaminated material with threat to human health or the environment (e.g., soil with concentrations above ten times the TAGM levels) will be disposed off-site. Waste disposal companies and disposal facilities will be identified in the SS-WP. All waste manifests will be reviewed by Parsons project manager as documentation of the disposal activities.

In instances where only a monitoring well was installed, with no soil sampling performed, the disposal of the soils generated during well installation will be the same as the disposal option for the groundwater (i.e. groundwater requires off-site disposal, therefore soils from associated well installation will also be disposed of off-site).

The disposal of excavation spoils will be addressed on a site by site basis and will be addressed in the site-specific SAP.

With prior permission from the Seneca County Sewer District, recovered groundwater from an excavation, the water collected from decontamination operations, and other waters generated during construction will be collected and stored in tanks for on-site storage and analytical sampling, before being discharged to the Seneca County Sewer District No. 2 via an on-site sanitary sewer. Required permits will be obtained before discharging. All waters will be appropriately tested and approved for discharge prior to release.

16.3.13 Corrective Action

A corrective action shall be initiated during the field work when changes are made in the field that do not meet the scope of work requirements or other conditions are identified that are not consistent with the SAP or SS-WP. Section 11.1 describes corrective action procedures for field activities.

16.3.14 OE/UXO Sites Sampling, Investigation, and Removal Action

This section presents a summary of the practices and procedures Parsons will use to perform sampling, investigation, and OE/UXO removal at potential OE/UXO sites at the Seneca Army Depot. Training and certification requirement for field staff working at potential OE/UXO sites are presented in Section 14 of the SAP. The health and safety requirements for working at potential OE/UXO sites are presented in the Parsons (2005) Accident Prevention Plan and Generic Site-Wide Health and Safety Plan for Seneca Army Depot Activity. SOPs for activities associated with OE/UXO investigations are attached in **Appendix H**. SOPs for other geophysical survey activities (e.g., EM-31) are provided in Section 16.3.3.

16.3.14.1 Geophysical Prove-Out

The geophysical prove-out will be required at the beginning of any OE/UXO investigation to demonstrate the capabilities of the geophysical equipment and personnel being employed during the removal action. The prove-out grid will contain several items buried by Parsons and USACE. The data will be used to evaluate the positioning and noise level produced by the array. The main purpose of the data collected over the prove-out grid is to demonstrate that the equipment and procedures used can meet the project requirements. Therefore, prove-out activities will use all proposed geophysical data collection methods. The main variables in the proposed methods are the instruments used in the data collection and the method of positioning the equipment. The method recommended based on the previous experience at Seneca is time domain EM acquisition using a three-sensor EM61-MK2 towed array and a Schonstedt™ magnetometer, as shown in the table below.

EQUIPMENT AND POSITIONING METHODS

Geophysical Instrument	Positioning Method
Schonstedt™ Magnetometer	Fiducials using local coordinates
Schonstedt™ Magnetometer	Real Time Kinematic (RTK) GPS positioning
EM61-MK2 Three-Sensor Towed Array	RTK GPS positioning
EM61-MK2 Hand-pulled System	RTK GPS positioning

Both types of instruments (Schonstedt™ magnetometer and EM61-MK2) will be used to collect data across the existing grid, and the results will be processed in an identical manner to that which will be used for the clearance surveys, ensuring that the final product of the geophysical survey will meet the project objectives. The results of the prove-out analysis will be summarized in a letter report and provided to the Army within one week of completion of the data acquisition over the prove-out grid.

16.3.14.2 Explosives Management Plan

The Explosives Management Plan (including acquisition, inventory, storage, transportation, and disposal of explosives) is presented in **Appendix H** of this SAP.

16.3.14.3 SOPs for Dynamic Events

Dynamic events such as rain and solar flares may affect geophysical data collection. Procedures for geophysical survey operations when these events occur are presented in this section. SOPs for operations under other severe weather conditions can be found in the SOP for Severe Weather Operations in **Appendix H**.

Rain

The effect of rain on geophysical operations is primarily dependent on the instrument being used and the physical site conditions (terrain and vegetation).

- Instrument: Most of the instruments commercially available are relatively water resistant. Additional measures will be taken by the survey teams (such as covering connections with plastic sheeting) to reduce the possibility of moisture impacting the instrument's electronics. When possible, survey teams will operate the instruments under very light rain conditions (drizzling). If the rain persists and the survey team leader determines that there is a potential for an impact to the data quality or that moisture could be getting into the instrument, field operations will cease and the project geophysicist will be notified. Operations will continue after the rain has ceased or has reduced to a drizzle.

- Site Conditions: At sites where footing for the operators becomes difficult because of wet terrain or vegetation, operations will cease until the area is deemed safe by the UXOSO. The determination to stop will be made by the UXOSO, and the project team will be immediately notified.

Solar Flares

Solar flares are sun-generated phenomena, typically occurring in the afternoon, which may temporarily generate high-magnitude magnetic noise sufficient to make magnetometers, often gradiometers, and occasionally electromagnetic sensors unusable for the duration of the event. Solar flares are typically readily observable by the instrument operators as rapidly fluctuating signal readings with no apparent cultural or survey source. The PM will be alert to solar flares and temporarily cease data collection until static testing shows a cessation of the solar activity. The PM will log the time intervals when solar flare activity is observed to help determine whether any data (for digital geophysics) have been affected. The National Oceanic and Atmospheric Administration maintains a helpful website at http://spaceweather.com.

16.3.14.4 Site Clearance

Surface preparation (also referred to as "Surface Avoidance") entails the visual inspection of each clearance area for metal ordnance-related items and scrap. This activity should be performed immediately following establishment of a geophysical survey and before any subsurface anomaly investigation. Surface preparation operations will be performed by field teams consisting of two UXO technicians and four sweep personnel. Operations will be initiated by establishing a linear array with the five team members along the southern boundary of a survey grid. The first member in the array is positioned at the southwest corner of the grid. The remaining four members are spaced to the east at 5-foot intervals. Upon assembly, the members of the array proceed in a straight line toward the northern boundary of the survey grid. Based on the 5-foot spacing, each member visually surveys a 5-foot wide path. The team's leader follows the array to ensure that the array moves forward in unison and that the 5-foot spacing is maintained. Additionally, the team leader collects all identified MPPEH related items and scrap from the survey grid. Operations for surface sweep and vegetation removal will be performed in accordance with the SOP for Chipper Operations and the SOP for Mechanical Vegetation Removal, as attached in **Appendix H**.

16.3.14.5 Geophysical Investigation

Unless otherwise specified by the SS-WP, land-based geophysical survey methods will be utilized to identify and remove MPPEH at the Seneca Army Depot. These surveys will be conducted using Schonstedt™ magnetometers and the EM61-MK2 towed array system. Surveys employing Schonstedt™ magnetometers, the EM61-MK2 towed array, and stand alone EM61-MK2 pedestrian

systems are hereafter referred to as "mag and flag," "towed array," and "pedestrian mode" surveys, respectively. A field data sheet form is provided in **Appendix C**.

Geophysical Data Quality Objectives

The objective of the geophysical investigation is to accurately locate and record the locations of geophysical anomalies, which could be material posing an explosive hazard. The geophysical investigation areas and identified anomalies will be mapped for subsequent evaluation (including intrusive investigations of anomalies where geophysical signal strength and amplitude suggest the potential of UXO/MPPEH). In accordance with the USACE (2002) DID OE-005-05.01, the accuracy goal for 95 percent of reacquired geophysical anomaly locations is horizontally within a one meter radius of their original surface location as marked on the dig sheet (an example of dig sheet is provided in **Appendix C**). Horizontally, 95 percent of all excavated items will be within a 35-cm radius of the reacquired location. Secondary DQOs may be developed based on the geophysical prove-out results. Variations will be noted and if they cannot be addressed in the field (i.e. equipment replacement, change in vehicle speed, etc) then a root cause analysis memorandum will be generated. If there are more than 15% "false positives", a re-evaluation of the data, detection methods being utilized, and overall project QC shall be performed. A written response explaining the reason for the excessive false positive results and a Corrective Action Plan, if appropriate, shall be submitted to the Contracting Officer within 10 days of identification of the situation.

Mag and Flag

Mag and flag surveys will be conducted in areas by UXO technicians or sweep personnel where the maneuverability of the EM61-MK2 is limited, for surface clearance, and in the vicinity of structures. This type of survey requires operators using Schonstedt™ magnetometers to identify anomalies in the field (the "mag" portion of the survey). The mag and flag survey will be initiated by establishing a linear array of magnetometer operators along the southern boundary of a survey grid. The first member in the array will be positioned at the southwest corner of the grid. The remaining members will be spaced to the east at 5-foot intervals. Using Schonstedt™ magnetometers, each member of the array will proceed in a straight line toward the northern boundary of the survey grid. Each magnetometer operator surveys a 5-foot wide path. The team's leader (a UXO technician) follows the array to ensure that the 5-foot spacing is maintained and to verify identified anomalies. Locations of confirmed anomalies will be marked in the field with survey pin flags and recorded on a field. Data from these surveys are not recorded in a data logger, as they will be during surveys employing the EM61-MK2. The locations of these anomalies will be indicated on field data forms (i.e., dig sheets) produced after survey is completed. The marked locations can either be surveyed using a Robotic Total Station (RTS) survey system or be investigated by conducting intrusive investigative activities from a known point.

The Schonstedt™ magnetometer is a hand-held unit that employs two fluxgate sensors aligned and mounted a fixed distance apart to detect changes in the earth's ambient magnetic field caused by ferrous metal. The Schonstedt™ magnetometer responds with an audio output and a meter deflection when either sensor is exposed to a disturbance of the earth's ambient field associated with a ferrous metal target and/or the presence of a permanent field associated with a ferrous metal target. (In most cases, it will be a combination of both circumstances.) Schonstedt™ magnetometers, which are highly portable, will also be used during UXO avoidance activities and intrusive operations.

EM61-MK2 Surveys

The towed array system will consist of three EM61-MK2's attached to a platform constructed of structural fiberglass and other non-metallic pieces. It will be towed behind a small four- or six-wheel all-terrain vehicle (ATV) such as a John Deere Gator. Vehicles with a minimum of two seats are preferred so that the tasks of the driver and the geophysical equipment operator are performed by separate personnel. The selection of the vehicle will be critical as some small ATVs produce significant amounts of electromagnetic noise. The amount of such noise will be tested prior to the beginning of the survey. The array will be positioned using a GPS with RTK accuracy, such as the Trimble® 5700 or equivalent.

The EM61-MK2 operated in "Pedestrian Mode" will be used in areas inaccessible to the towed array such as the transects or the smaller areas the towed array cannot cover. The EM61-MK2 system operated in pedestrian mode coil will be positioned using local coordinates and fiducials to segment the data collection.

The data for the EM61-MK2s and the Trimble® 5700 system will be recorded on a laptop computer located on the tow vehicle via RS-232 ports. The data will be recorded using the Geometrics Maglog software. This program will record all four data streams (three EM61s and a GPS system) on hard disk, time-stamping them with the computer time. This common time stamp will ensure that all data are tied to a single consistent set of times and will remove the need for synchronization between the EM61-MK2 data logger clocks and the GPS clock as well as eliminating the effects of clock drift between the various instruments.

Maglog also graphically displays the data on screen to provide the operator with the feedback regarding the instrument operation. Visual and audible warnings can be configured for the software so that the geophysical equipment operator will be immediately aware if any of the elements of the towed array are not functioning optimally.

Maglog records the data in the raw form that it receives from the serial port on the laptop hard disk in a separate file for each data stream (three EM61 MK2 files and one RTK GPS file). After the completion

of each day (or more often as needed), the data will be transferred to the data processing computer. A single day's worth of data is expected to be on the order of several hundred megabytes.

Subsequently, the GPS will be filtered using Parsons proprietary software to remove GPS data that do not meet required positional quality tests. The filtering will be based on the positional type of each point (i.e. RTK, differential GPS, uncorrected), position dilution of precision (PDOP), and apparent velocity between points. Points that are within a specified radius from each other will also be discarded. This removes artifacts from the processed data that can results from the array "spinning" when the array is actually stationary. Small variations in the location of the array can cause the software to believe that the array is traveling in a small circle, introducing positional errors into the calculation. Removing points that are too close together removes this type of error without any decrease in the positional accuracy of the algorithm. The filter also removes records corrupted during transmission from the GPS unit to the laptop. While these corrupted data transmissions rarely occur, they can introduce significant positioning errors in the processed data.

After filtering, the complete data set is imported into Geometrics Magmapper software. This software merges the EM61-MK2 data and the GPS data to position the geophysical data. The user inputs the offset from the center of the GPS antenna to the centers of each of the three coils to position the data recorded from each of the coils. Magmapper positions the data using these offsets and the computed bearing of the GPS data. The data are then exported in Geosoft ASCII XYZ format. The exported data will include positional information in latitude-longitude format, the data from each of the four channels for each coil, battery voltage, other equipment status information, and the time stamp derived from the laptop.

This data will then be imported into the Geosoft Oasis montaj™ geophysical data processing environment using a custom script written specifically for this project. The script will automate the process for importing the data, converting the positions to New York Central State Plane coordinates and automatically leveling the data using the UX-Detect drift correction algorithm. In addition, a sum or weighted average of the four channels is calculated for use in later processing.

The static tests are then evaluated for compliance with the requirements specified in the USACE (1986) DID OE-005-05. Any spikes present in the data are manually edited. The geophysical processor then evaluates the results of the latency test to determine the instrument latency correction necessary for the data set. This corrects for delays that occur in the electronics of the EM61-MK2s and in the processing of the data on the data recording computer. The latency correction is computed on a sensor-by-sensor basis by determining the latency value that overlaps the anomaly due to the latency test item when the array travels over the anomaly in different directions. Typically this value is between 0.2 and 0.4 seconds.

Once the latency value is determined, it is applied to the whole data set, and the sum or average channel is gridded and displayed. The display is evaluated against the information in the field notes to determine if they are consistent and whether or not the data meets expected data quality standards.

Anomaly Selection

The processor will automatically make anomaly selections on the data using the Geosoft UX-Detect Blakely algorithm. This will be done in accordance with the threshold anomaly selections as determined from the prove-out analysis. These anomaly selections will then be evaluated to determine if the response from all four channels decays in a manner consistent with an anomaly due to a buried metallic object. If not, the anomaly will not be intrusively investigated. This evaluation has proven useful in decreasing anomaly selections of noisy data and peaks that result from gridding artifacts that can arise from closely spaced lines. The remaining anomaly selections will then be merged so that closely spaced anomaly selections will be consolidated to single pick. The anomaly selections and the data will then be evaluated by the geophysical processor to ensure that the remaining anomaly selections are valid. Anomaly selections around surface features identified in the field notes will be removed. The processor can also add or delete any other anomaly selections that the processor feels necessary.

Anomaly Reacquisition

For towed surveys, anomalies will be identified through geophysical data analysis. Anomalies will be selected for intrusive investigation based on review of the geophysical surveys, accumulated anomaly patterns, strength of the geophysical signal, and professional judgment. A dig sheet listing all selected anomalies with their respective local and New York State Plane coordinates will be prepared for each grid surveyed. For mag and flag surveys, geophysical anomalies will be identified in the field during the survey process. Locations of confirmed anomalies will be marked with survey pin flags and recorded on a dig sheet.

The following steps will be performed to re-acquire the location of the selected anomalies:

- A geophysical reacquisition team will use an RTK system, RTS, or measuring tapes to determine the location of the anomaly from the grid corners. The ground will be painted at the measured location of the suspected anomaly.

- The geophysical reacquisition team will use a Schonstedt™ magnetometer or EM61-MK2 for reacquiring geophysical anomalies. If the anomaly is found within 1 meter of the painted location, a pin flag will be placed at the actual anomaly location. The signal response, offset distance, and direction from the re-acquired location will be noted on the dig sheet.

Anomaly reacquisition and marking procedures should be consistent with the USACE (2002) OE-005-05.01.

Instrument QC Tests

It is imperative to perform and review QC tests before carrying out production geophysical work. This ensures that the geophysical system is functioning properly and optimized for the target objectives. All instrument used in the geophysical survey should be tested in accordance with the quality control frequency specified in the USACE (2002) DID OE-005-05.01 and meet the acceptance criteria documented in this guidance. Table 24 provides the quality control frequency and acceptance criteria chart provided in the USACE (2002) guidance.

At the beginning of each day, the operator will let the instruments warm up, check the sensor positions, and check all connections including a cable shake test. Heading Error Tests will be conducted during the first day of the project for magnetometer. If equipment is replaced during the course of the site activity, the new equipment will be standardized and used to collect data over the prove-out grid. The towed array will acquire data over the prove-out grid, with the results compared with the hand-pulled system to verify the operation of the towed array system.

The six-line test will be conducted to evaluate different equipment parameters and will only need to be done once during the project for each instrument. The six-line test will be conducted to evaluate the repeatability and positional accuracy of the response amplitude of a ferrous object. The EM61-MK2 will be hand pulled between two wooden stakes placed 100 feet apart, with a marker at 50 feet. The test object will be placed at 25 feet. The operator will walk between the stakes six times and mark a fiducial at 50 feet. The first time will be with no spike object present; the operator will walk slowly the fifth time and the quickly sixth.

The six-line test will be repeated using the towed array to evaluate the repeatability and positional accuracy of the response amplitude of a ferrous object. The test object will be placed at a known location (i.e., southwest corner of the prove-out grid). The towed array will be driven over the test object six times. The first time will be with no spike object present; the operator will drive slowly the fifth time and quickly the sixth. This will allow a latency correction to be determined for the towed array.

At the beginning and end of each day, each instrument will complete a static test. This test is done by parking the instrument and collecting background data for three minutes. Subsequently a metallic object will be placed within the center of each sensor and data recorded for one minute. This procedure is repeated until data have been collected with the spike object located in each of the three sensors.

A latency test will be conducted at least twice a day by driving the array over three buried objects. The objects are arranged in a diagonal line so that when the array is driven over them in orthogonal directions, each object will pass directly underneath only a single sensor. This will allow determination of the latency value for each sensor individually. The location of these objects will be surveyed in so that the absolute positioning system can be verified by comparing the final locations of the anomalies with the known locations of the buried objects. It is expected that the anomaly peaks will be located within 1-foot of the actual buried object location.

Quality Control

Quality control will be performed during all stages of data acquisition, data processing, and target selection. The project geophysicist will be fully responsible for overseeing and documenting all QC performed with respect to the former Seneca Army Depot geophysical surveys.

Geophysical data associated with potential anomalies will be reviewed at several stages. The first quality check will be during data collection. The field crews will check the data logger to ensure that data is being collected and will examine the data during data logger "dumps" when the information is downloaded to the hard drive of a portable computer. A second quality check will be performed when the data is evaluated. If the coordinates of the data do not fall within those of the area investigated, Parsons will become aware of this when loading the data for evaluation. A final quality check will occur during the intrusive investigation, when the findings are compared against the interpretation of the geophysical data. Efforts will be made to automate the checking of the DQOs within Geosoft and the values. If the discrepancies cannot be addressed by fixing equipment or procedures in the field than a root cause analysis of the discrepancy will be generated and submitted to USACE representatives.

16.3.14.6 Data Management and Mapping

Geophysical data shall be managed in accordance with the specifications outlined in the USACE (2002) DID OE-005-05.01.

There is no digital data associated with the Schonstedt™ magnetometer; therefore, no electronic data management will be necessary for mag and flag survey.

Digital towed array survey data collected in the field will be stored electronically on field laptop or personal computers. Raw field data will be backed-up onto CD-Rs and kept separate from the CD containing the data from the day-to-day operations. This data will be stored in ASCII data files whose names will reflect the access road, sector, and homestead number. The file extension will be "xyz." A weekly back up of all data will be performed via CD.

Raw field data also will be transmitted to the USACE Geotechnical Branch within a reasonable time after it has been acquired. The data will be placed on a Seneca Army Depot FTP site as well as being transmitted on CD to the USACE. This data will be transmitted to USACE every Monday morning or the next business day if Monday falls on a holiday. The format of the raw and final processed field data from the EM61-MK2 will be in column-delineated ASCII files in the format X, Y, V1, V2, … where X = easting coordinate, Y = northing coordinate, V1 = top coil reading, and V2 = the next lower (spatially) co-located coil reading. The data will be in the New York Central State Plane coordinate system. No comment or survey line identification will be provided in the data files transmitted to USACE. The file names will reflect the sector number and grid number for the data being transmitted. A text file will be transmitted with the raw field data explaining all processing that was performed on the data and detailing any data issues identified by the geophysical field personnel. A CD that includes all data maps produced and the associated reports shall be delivered with each copy of the report.

All final mapping will be generated using GIS and provided to the USAESCH, USACE-New York, Seneca Army Depot in ESRI Arc View digital design files on a CD-ROM. All data characteristics (e.g., file naming and relationships, level structures, colors, line styles, weights) will be compiled in the design files in accordance with the surveying and mapping requirements of the Tri-Service Spatial Data Standards. Site maps plotted from these design files will be provided on reproducible drawings. The size of these drawings will be based on the information to be displayed.

The location, identification, and coordinates of the control points will be plotted on the reproducible maps (the surveyors-control points will be provided to the USACE-New York in digital format). Each map will include grid orientation to true north and magnetic north, with the differences between them shown in minutes and seconds. Grid lines or tick marks in feet and at systematic intervals will be shown with their grid values on the edges of the map. A legend showing the standard National Geodetic Survey symbols used for the mapping, a map index showing the site in relationship to all other sites within the boundary lines of the project area, a border, and a standard USACE title block also will be shown on each map.

16.3.14.7 UXO Demolition

During demolition of UXO/MPPEH and related material, safety is the primary concern. The most obvious requirements are to protect personnel, the public, and the environment from fire, blast, noise, fragmentation, and toxic releases. Planned detonation of explosives requires more stringent safety distance requirements than those for ordnance in storage, and shall be conducted in accordance with the requirements outlined in USDoD (2004) DoD Ammunition and Explosives Safety Standards (DoD 6055.9-STD).

Control of the demolition site must be maintained during demolition operations. All personnel who are not essential to demolition operations must evacuate to a safe area. Access roads entering the blast area will be blocked outside the Maximum Generated Fragmentation Distance (MGFD) during explosive disposal operations to ensure that unsuspecting individuals are not placed in jeopardy by the explosion. The SUXOS will assure the area is clear of unauthorized personnel and equipment prior to permitting attachment of the initiation devices to the priming charge. Fragmentation distances and overpressure distances are based upon the US Army Engineering and Support Center, Huntsville (USAESCH) calculations for the MGFD presented in the Explosives Safety Submission (ESS). The calculation of fragmentation and overpressure distances is important to ensure the safety of not only site personnel but also the public. The initial fragmentation distance for this removal will be in accordance with the explosives sitting requirements set forth in the ESS. UXO/MPPEH that cannot be moved (e.g. fused or hazardous items) must be Blown In Place (BIP).

The on-site demolition shall be under the direct control of an experienced and trained UXO Technician III charged with the responsibility for all demolition activities within the area. The SUXOS shall be responsible for training all personnel regarding the nature of the materials handled, the hazards involved, and the precautions necessary and shall be present during all on-site disposal operations. The demolition team leader will maintain custody of the blasting machine or fuse igniters. The SUXOS shall ensure that the appropriate local authorities are notified prior to daily on-site demolitions.

The Parsons site manager or UXOSO will coordinate with the Seneca Army Depot Program Office upon mobilization in order to facilitate detonation reporting procedures. The UXO team and the UXOSO will evaluate the UXO and either detonate it in place (i.e. BIP) or relocate the ordnance to a designated area within the grid survey area. Detonations will occur only after all unnecessary personnel have left the area, road guards have been posted, and the required Seneca Army Depot Project Office personnel have been notified.

All of the Removal Action locations should be within the limits of Seneca Army Depot. If the Maximum Fragmentation Radius exceed the boundary of Seneca Army Depot than Engineered Controls will be used to mitigate the blast pressure and fragmentation of the disposal shot.

All demolition/disposal operations will be conducted in accordance with the Demolition SOP found in **Appendix H** of this work plan.

16.4 ENVIRONMENTAL SAMPLE COLLECTION

This section prescribes procedures for environmental sample collection activities. Decontamination shall be conducted in accordance with Section 16.3.11. For potential OE sites and sites with radioactive contamination, all any field activities should be conducted in accordance with the Generic Site-Wide Health and Safety Plan for Seneca Army Depot Activity (Parsons, 2005). Parsons pre-drilling protocol as described in Section 16.3.2 will be implemented before any drilling/excavation activity.

The construction material (e.g., plastic, PVC, metal) of the sampling devices described below shall be appropriate for the evaluation of target compounds identified for the project and shall not interfere with the chemical analyses being performed.

All purging and sampling equipment shall be decontaminated according to the specifications in Section 16.3.12 of this SAP prior to any sampling activities and shall be protected from contamination until ready for use.

16.4.1 Groundwater Sampling – Low Flow Purging and Sampling from Monitoring Well

Groundwater sampling for monitoring wells and microwells will be performed according to the Ground Water Sampling Procedure Low Stress (Low Flow) Purging and Sampling (USEPA Region 2, 1998). Low flow methods will be used to ensure collected samples are representative of groundwater conditions at the site. It should be noted that in the past high turbidities in the groundwater samples collected from monitoring wells at SEDA produced overstated groundwater results. Therefore, it is important to use low flow methods to collect groundwater samples from monitoring wells at SEDA. It should be noted that low flow sampling is not applicable in certain situations, such as bedrock wells with long open boreholes in which the water bearing zones have not been characterized. SOPs for groundwater sampling methods other than the low flow methods, if warranted, will be specified in the SS-WP.

The USEPA Region 2 (1998) recommended procedures will be implemented at the field to collect groundwater samples from monitoring wells. The USEPA Region 2 recommended procedures are presented in Appendix F and are briefed summarized below. SOPs for filtering water samples are presented in Section 16.4.12.

Unless otherwise specified in the SS-WP, groundwater samples should be collected in sequence from least to most contaminated well, whenever feasible, to minimizes the possibility of introducing contaminants into cleaner aquifers or areas.

16.4.1.1 Equipment

- Sample collection equipment (pumps, controller, safety cable, Teflon® tubing, generator, gas, polypropylene rope, buckets, graduated level etc.)
- Well construction data, location map, field data from last sampling event, sample analysis request forms
- Reagents for sample preservation, if sample containers not pre-preserved by the laboratory
- Appropriate sample containers
- Ice or ice packs
- Sample cooler
- Monitoring instruments (PID)
- Field instrumentation for on-site measurements (e.g., pH, conductivity, dissolved oxygen, oxidation reduction potential, turbidity meters, volatile organic compound monitor)
- Appropriate field and trip blanks and analyte-free water
- Sampling Records, Chain-of-Custody forms and sample bottle labels
- Security lock keys
- Tools (e.g., screw drivers, hammers, chisels, pipe wrenches with chain, tape measure)
- Electronic water level indicator
- Pocket calculator, wristwatch/time
- Field log book
- Groundwater sampling record (Appendix C)
- Indelible ink marker
- Clean plastic sheeting and 5-gallon bucket
- Paper towels and trash bags
- Decontamination supplies and reagents: Alconox (or equivalent), gloves (latex, nitrile, or scrub brushes equivalent), brushes, and
- Health and safety equipment

16.4.1.2 Field Procedures

1. Planning documentation and equipment. A list of documentation and equipment is listed in the USEPA Region 2 (1998) SOP, as attached in Appendix F.

2. Decontaminate the sampling equipment. SOPs for sample tubing and submersible pump decontamination are presented in Sections 16.3.11.3 and 16.3.11.4, respectively.

3. Check the well, the lock, and the locking cap for damage or evidence of tampering. Record observations. Data regarding groundwater sample collection will be recorded on the Groundwater Sampling Record (Appendix C).

4. Place sheet of polyethylene around wellhead for placement of monitoring and sampling equipment.

5. Measure VOCs at the rim of the unopened well with a PID and record the reading.

6. Unlock protective casing and remove well cap.

7. Immediately after well cap removal, take an organic vapor reading at the rim of the opened well using a PID and record reading in the field logbook.

8. Measure water level distance from top of casing and sound the total depth as detailed below. Record in logbook (a Groundwater Elevation Report form is included in Appendix C). Check tip of water level indicator for silt or product residue (if either are observed note in logbook).

    a. Lower decontaminated water level indicator into monitoring well until indicator sounds and light is illuminated.

    b. Confirm that the water surface has been contacted by repeatedly raising and lowering the indicator at least three times to ensure a consistent sounding level has been reached.

    c. Measure and record depth (nearest 0.01 feet) to the water surface from the top of casing in field logbook. The groundwater depth should be measure to a reference point of the top casing (usually a V-cut or a permanent black mark). If the well does not have a reference point, make one.

    d. Lower the indicator to the well bottom and record the total depth.

    e. Retrieve and decontaminate water level indicator.

9. Lower decontaminated low-flow purging device (pump, safety cable, tubing and electrical lines) into well within the screened area of the well producing the highest flow rate. The pump intake should correspond to the mid-point of the most permeable zone in the screened interval. The pump intake must be kept at least two feet above the bottom of the well to prevent disturbance and resuspension of any sediment or NAPL present in the bottom of the well.

10. The water level will be measured again, with the pump in the well, before starting the pump.

11. Begin pumping at 200 to 500 milliliters per minute (ml/min) and measure the groundwater elevation approximately every five minutes to ensure that the aquifer is not being stressed. Ideally, the pump rate should cause little or no water level drawdown (drawdown of 0.3 ft or less) in the well; and, if necessary, pumping rates will be reduced to the minimum capabilities of the pump to avoid pumping the well dry and/or to ensure stabilization of indicator parameters. If significant draw down occurs, reduce the pumping rate. All development and purge water will be contained in 55-gallon drums and disposed in accordance with Section 16.3.12.

12. Observe and record: odor, color, clarity, turbidity and general water condition in logbook. Also record changes in the physical condition of the monitoring wells that could affect the well integrity. Monitor indicator parameters (Temperature, pH, turbidity, and specific conductivity of the groundwater quality) approximately every five minutes during purging of the well using calibrated instruments (see Section 6). It is anticipated that the instruments used will be the Lamotte 2020 Turbidity Meter and the Horiba U-22. The well is considered stabilized and ready for sample collection when at least one well volume has been removed and the indicator parameters have stabilized for three consecutive readings as follows:

    a. $\pm$ 0.1 for pH;

    b. $\pm$ 3% for conductivity;

    c. $\pm$ 10 mv for redox potential;

    d. $\pm$ 10% for DO; and

    e. $\pm$ 10% NTUs for turbidity with the turbidity below 50 NTU (10 NTU or below is preferred).

    If the above stabilization parameters can not be met, and all attempts have been made to minimize the drawdown, check the instrument condition and calibration, purging flow rate and all tubing connections to determine if they might be affecting the ability to achieve stable measurements. All measurements that were made during the attempt must be documented. The sampling team leader may decide whether or not to collect a sample or to continue purging after five well volumes or five volumes of the screened interval. After the monitoring well is purged, do not turn off the pump or remove it from the well. Groundwater sample collection using the low-flow method is as follows:

13. Purge the monitoring well as described previously. After purging the well, the sampling team will change to new outer gloves for sample collection.

14. The groundwater sampling order is as follows: 1) volatile organic compounds, 2) semivolatile organic compounds, 3) herbicides, 4) pesticides and PCBs, 5) explosives, 6) phenols, 7) total metals

(preserved) 8) cyanide, 9) sulfate and chloride, 10) nitrate and ammonia, and 11) radionuclides. Collect groundwater samples for volatile analyses first, before any of the other parameters of interest. The actual sampling flow rate for volatiles must be accomplished with a gradual reduction in the flow rate down to 100 milliliters per minute and such that the drawdown of the water level within the well does not exceed the maximum allowable drawdown of 0.3 ft and that hydraulic head pressure is sustained within the sampling tube to reduce aeration, bubble formation, turbulent filling of sample bottles, and loss of volatiles due to extended residence time in the tubing.

A gradual reduction in association with sustained hydraulic head pressure will minimize aeration, bubble formation, turbulent filling of sample bottles, and loss of volatiles due to extended residence time in the tubing. Hence, this coincides with the USEPA Region 2 (1998) Low-Flow Purging and Sampling Procedure and the RCRA Groundwater Monitoring Technical Enforcement Guidance Document (OSWER Directive #9950.1, September 1986), which states that when collecting samples where volatile constituents are of concern using a bladder pump, pumping rates should not exceed 100 mLs/min. If problems are encountered trying to maintain a uniform 100 mLs/min flow rate during sampling, the inside diameter (I.D.) of the sampling tube will be reduced as it reaches the well head to ensure hydraulic head pressure is maintained. A reducer coupling (0.5 inch to 0.25 inch) will be installed approximately six feet from the actual sample port. Proper fitting installation, including the use of Teflon® tape, will eliminate connection problems. VOC samples will be collected in a manner that will minimize the loss of volatile compounds and will be collected directly into pre-preserved sample containers.

In some very low-yielding formations it may not be possible to sample with minimal drawdown even using low pumping rates. It should be noted that if the water level will not stabilize at minimum pumping rates and the water level is drawn down below the top of the pump, then stabilization of the indicator parameters may not be possible. In the past, these wells have been pumped to dryness and sampled as soon as they recovered sufficiently. Approval to sample in this manner will be required from the project manager, task manager, or site manager.

15. The sample discharge for all other analytical parameters can be a continuous flow of up to 250 milliliters per minute. All sample containers should be filled with minimal turbulence by allowing the groundwater to flow from the tubing gently down the inside of the container. To decrease the sampling collection time for other parameters, a 0.5-inch coupling and tubing should replace the reducer coupling and 0.25-inch tubing. Therefore, a stoppage in flow could occur after the collection of volatile organic samples in order to change the coupling/tubing. If field filtering is required, an in-line 45-micron filter will be inserted into the sample intake line.

16. After the sample bottle is filled, the cap will be placed on the bottle and the bottle will be packaged for shipment as specified in Section 5.3.

17. Collect QA/QC samples as specified in SS-WP.

18. Measure conductivity, pH, turbidity, DO, redox potential, and temperature after sample collection and record in the field logbook.

19. Remove pump and tubing. Pump will be decontaminated for use for the next well and tubing will be discarded in accordance with Section 16.3.12.

20. Measure and record well depth.

21. Close and lock the well.

Field crews should take cautious while collecting groundwater samples to avoid contamination. A polyethylene ground cloth and 5-gallon bucket will be placed beneath all sampling equipment during well purging and sampling to prevent the spread of contaminated groundwater, and if a gas-powered generator is used to drive the pump motor or controller, the generator must be placed a minimum of 25 feet downwind of the well to limit the incidence of cross-contamination during sampling. Low flow centrifugal or bladder pumps constructed of stainless steel or Teflon® and Teflon® tubing will be used for groundwater sampling at SEDA. Each well will have its own dedicated tubing.

16.4.2 Subsurface Soil Sampling With Standard Hollow-Stem Auger Drilling Rig Equipment

This section provides procedures for subsurface soil sampling with standard hollow-stem auger drilling rig or similar device. The objective is to ensure a representative subsurface soil sample is collected at each designated sampling location.

16.4.2.1 Equipment

- Sample location map, sample analysis request forms
- Reagents for sample preservation, if sample containers not pre-preserved by the laboratory
- drilling rig capable to drilling to the appropriate depth
- 4 1/4-inch or 6 1/4-inch I.D. hollow stem augers
- Split Spoon Samples: 2-inch and/or 3-inch, 2-foot-long carbon steel split spoons
- FID or PID (e.g., OVM)
- Folding ruler
- Field table
- Tin foil
- Ball jars with lids
- Field log book

- Indelible ink marker
- Overburden boring report and soil sampling record forms (Appendix C)
- Laboratory sample containers
- Sample coolers
- Ice or ice packs
- Stainless steel spatula
- Stainless steel sample bowls
- Sampling Records, Chain-of-Custody forms and sample bottle labels
- Clean plastic sheeting and 55-gallon drum for soil
- Pocket calculator, wristwatch/time
- Paper towels and trash bags
- Decontamination supplies and reagents: Alconox (or equivalent), gloves (latex, nitrile, or scrub brushes equivalent), brushes, and
- Level D health and safety equipment as described in the site-specific Health and Safety Plan.

It should be noted that soil with low level VOCs may be sampled one of two ways, either collected in sample jar or as an EnCore™ sample (modified Method SW-846 5035). USEPA Region 2 (2001) requires the EnCore™ sampler. Unless otherwise specified by the SS-WP, three Encore samples will be collected at each location.

16.4.2.2 Field Procedures

A stainless steel split spoon sampler will be used to collect subsurface soil samples in borings using a drilling rig, using the following procedure:

1. Determine and clear (for utilities) the boring location through the depot as described in Section 16.3.2.

2. Surface materials such as vegetation may be removed from the boring location.

3. A minimum 2.5” inside diameter hollow stem auger will be used to advance the borehole to the desired subsurface depth.

   Sample depth will be specified in the SS-WP. Typically, three samples from each boring will be selected for chemical analysis: 1) 0 to 12 inches below grade; 2) immediately above the water table; and 3) between samples (1) and (2). The intermediate sample will be collected at a depth where one of the following site specific items occurs: (1) a stratigraphic change such as the base of the fill, (2) evidence of perched water table, (3) elevated PID readings, or (4) visibly affected soil (e.g., oil stains). If none of these occur, then the intermediate sample will be collected at the

halfway point between the samples collected at the surface and at the water table. If intermediate split spoon samples exhibit elevated PID readings, the one with the highest concentration will be chosen as the intermediate sample.

4. Once the desired sampling depth has been reached, a decontaminated standard three-inch diameter, two-foot long carbon steel split spoon barrel will be used to retrieve the subsurface soil sample. Split spoons of 2-inch diameter may be used only if the same interval will not be selected for chemical analysis. Immediately after the opening of a split spoon sampler the contents of the sample will be screened for VOCs and, if necessary, radiation. One to three readings will be taken along the sample with additional readings taken if additional distinctive zones are observed. These data will be recorded in the appropriate locations on the Overburden Boring Report form (Appendix C). Descriptions of the sample will also be entered on the form.

5. A new pair of clean disposable latex or nitrile gloves will be donned at each sampling location.

6. The split spoon sampler will be brought to the surface, and opened for sample collection and lithological description.

7. Collect samples to be analyzed for volatile organic compounds first in two 40 milliliter (ml) vials with septum seals. These soil samples will not be homogenized or composited during the sampling process. All VOA sample bottles will be completely filled, leaving no void space. For samples to be analyzed for other fractions, place the sample aliquot in a decontaminated stainless steel bowl, homogenized with a decontaminated stainless steel utensil using the quartering method (see below), and then fill the remaining sample containers in order of reverse volatility. Sampling information will be recorded on the Soil Sampling Record (Appendix C). This form includes information such as the sample location, number, depth, time, description, and QA/QC sample names.

8. Once the samples have been collected, they will be packaged as specified in Section 5.3.

9. QA/QC samples will be collected as specified in SS-WP.

10. Backfill the boring with the soil removed from the hole, place bentonite on the top of the backfilled hole, and restore the boring location to its original condition.

The cut and quartering technique is as follows:

The sample will be thoroughly mixed in a bowl, and divided into quarters. A portion of the soil will be gathered from two of the quartered sections. This process will be repeated until the amount of soil needed to completely fill the sample containers has been obtained. It is very important that the soil samples be mixed as thoroughly as possible to ensure that the sample is representative of the interval sampled.

16.4.3 Surface Soil and Dry Sediment Sampling

This section provides procedures for surface soil and dry sediment sampling. Sampling representativeness should be maximized by collection of composite samples unless regulatory agencies refuse to accept composite sample data. SS-WPs should specify compositing scheme. The objective is to ensure a representative soil or sediment sample is collected at each designated sampling location.

16.4.3.1 Equipment

- Sample location map, sample analysis request forms
- Reagents for sample preservation, if sample containers not pre-preserved by the laboratory
- Appropriate sampling equipment (e.g., hand auger, stainless steel spoon, stainless steel spatula, stainless steel or Pyrex bowl)
- FID or PID (e.g., OVM), if warranted
- Folding ruler
- Field table
- Tin foil
- Ball jars with lids
- Field log book
- Indelible ink marker
- Surface soil/sediment sampling record forms (Appendix C)
- Laboratory sample containers
- Sample coolers
- Ice or ice packs
- Sampling Records, Chain-of-Custody forms and sample bottle labels
- Clean plastic sheeting and 55-gallon drum for soil
- Pocket calculator, wristwatch/time
- Paper towels and trash bags
- Decontamination supplies and reagents: Alconox (or equivalent), gloves (latex, nitrile, or scrub brushes equivalent), brushes, and
- Health and safety equipment as described in the site-specific Health and Safety Plan

16.4.3.2 Field Procedures

Surface soil and dry sediment samples will be collected from 0 to 2 inches unless an alternate depth is specified in the SS-WP. Surface soil and dry sediment samples will be collected using either a spoon (0-2”) or a hand auger (for depths greater than 2”) unless otherwise specified in the SS-WP. Listed below is the process for collecting soil samples:

1. A new pair of clean disposable latex or nitrile gloves will be donned at each sampling location.

2. Prepare the sampling location by removing all vegetation, roots, etc., from the sampling point.

3. Depending upon desired sampling interval, either spoon off the sample or advance a decontaminated hand auger to the desired sampling depth below ground surface.

4. For surface samples at greater than 2" depths, remove the hand auger from the boring and use a decontaminated stainless steel spoon to remove the sample from the auger boring.

5. Place the sample into a decontaminated bowl (stainless steel or Pyrex). After the soil to be sampled has been placed in the bowl, as much organic matter (roots, leaves, worms, etc.) as possible shall be removed from the bowl.

6. Once enough sample has been collected, homogenize the sample thoroughly, using at a minimum the quartering method described in Section 16.4.2.2. When the sample has been completely mixed, fill the sample containers in reverse order according to volatility. Care will be taken to ensure that the soil placed in the bowl is not agitated extensively during this process if volatile organic analysis samples are necessary. If VOA samples are necessary, they shall be collected first. All VOA sample bottles will be completely filled, leaving no void space. Following the collection of any VOA samples, the remaining soil shall be homogenized by mixing, and the rest of the necessary samples will be collected.

7. After the sample bottles are filled, the caps will be placed on the bottles. The collected samples will be stored in a chilled cooler until they can be sent to the laboratory for analysis. The samples will be packaged for shipment as specified in Section 5.3.

8. QA/QC samples will be collected as specified in SS-WP.

9. Backfill the boring with the soil removed from the hole and return the site to its original condition to the extent possible.

Sampling information shall be recorded on the Sampling Report form for soil (Appendix C). This sheet includes information such as the sample location, number, depth, time, description, and QA/QC sample names.

16.4.4 Surface Water Sampling

This section provides the procedures for collecting surface water samples. The objective is to ensure a representative surface water sample that is collected in such a manner as to minimize the introduction of

sediments into the sample is collected at each designated sampling location. If target analytes in surface water include metals, it is recommended that surface water samples be analyzed for hardness. SOPs for filtering water samples are presented in Section 16.4.12.

16.4.4.1 Equipment

- Site maps indicating the locations of samples, sample analysis request forms
- Specialized Sampling Devices (used in atypical situations): boat for sampling ponds, lakes, and rivers, if warranted
- Reagents for sample preservation, if sample containers not pre-preserved by the laboratory
- Sample bottles and sample labels
- FID or PID (e.g., OVM), if warranted
- QA/QC: Trip blanks and extra sample sets for collection of field blanks, duplicates
- MS/MSDs, MRD duplicates, and any other QA/QC samples
- Coolers packed with enough ice and/or cold packs to maintain sample preservation
- Sample Record forms and Chain-of-Custody forms
- Field log book, surface water sampling record form (Appendix C)
- Indelible ink markers, pens
- Pocket calculator, wristwatch/time
- Marker flags or stakes
- Paper towels and trash bags
- Clean plastic sheeting and 5-gallon buckets
- PPE: vinyl, neoprene, and/or nitrile gloves, Tyvek, Hip waders and/or waterproof boots, Level C equipment if necessary
- Deionized/Distilled water, paper towels, and trash bags
- Folding ruler
- Decontamination supplies and reagents: Alconox (or equivalent), gloves (latex, nitrile, or scrub brushes equivalent), brushes
- Field instrumentation for on-site measurements (e.g., pH, conductivity, dissolved oxygen, oxidation reduction potential, turbidity meters, volatile organic compound monitor), and
- Health and safety equipment as described in the site-specific Health and Safety Plan

16.4.4.2 Field Procedures

The surface water sample collection location should be deep enough so the sample bottles can be completely submerged (if possible), in an area with minimal flow or surface disturbance, and free of suspended material. Downstream samples will be collected first and disturbances during wading should be avoided. Time for surface water and sediment sampling will be specified in the SS-WP. Usually the

sampling will occur during high flow conditions (i.e., after a rain event) to assure sufficient water supply and to sample site stormwater runoff. At locations where both surface water and sediments will be collected, the surface water samples should be collected before sediment samples. The process for collecting surface water samples is as follows:

1. Prior to sampling at any surface water/sediment location, the direction of actual surface water flow directions shall be noted and recorded on a site map. The flow direction shall also be compared to the flow directions expected at the site to ensure that the samples planned for the downstream direction are truly at a downstream location.

2. A new pair of clean disposable latex or nitrile gloves will be donned at each sampling location.

3. Before the surface water samples are collected at each location, measurements of temperature, pH, specific conductance, turbidity, and oxidation-reduction potential (ORP) shall be taken by direct immersion of instrument probes into the water body. If direct measurement is not possible, these measurements shall be taken from water collected and placed in a field container. If this procedure is followed, the water used to analyze field parameters shall not be used as the sample water; another sample will be collected.

4. Facing upstream, submerge pre-labeled sample bottles in the upright position to prevent the loss of preservative into the water. Sediment should not be disturbed during the collection of surface water samples.

5. Allow sample bottle to fill and use bottle cap if necessary to fill the bottle completely. If samples cannot be collected directly into the sample bottle, a decontaminated sample collection device made of glass, stainless steel, or Teflon® (e.g., a bailer) may be used.

6. After the sample bottle is filled, the cap will be placed on the bottle and the samples will be packed in an ice-filled cooler immediately after sampling. The samples will be packaged for shipment as specified in Section 5.3.

7. Conductivity, pH, turbidity, and temperature, will be measured after sample collection. The measurements will be recorded in the field logbook. All pertinent field data will be recorded on the Sampling Record for Surface Water (Appendix C).

8. QA/QC samples will be collected as specified in SS-WP.

9. If filtered samples are required, a Grundfos pump will be used to pull the sample through an in-line 45-micron filter. The sample will be drawn directly from the surface water body, or from a sample aliquot collected into a laboratory-supplied, preservative-free sample bottle. The sample will be

discharged from the filter line outlet directly into laboratory-supplied pre-preserved sample bottles. Alternate methods, if used, will be described in the SS-WP.

16.4.5 Wet Sediment Sampling

Sediment samples should be collected from background or furthest from the source locations first, to minimize the possibility of cross-contamination. Thereafter, the most downstream sediment samples will be collected followed by the next upstream samples. If surface water samples are to be taken at the same location, they should be collected before the sediment samples.

Unless specified in the SS-WP, sediment sample shall be collected within 6 inches into the sediments. The Sampling Record form for surface water (Appendix C) can be used to record all pertinent information. The description will be recorded according to the procedures outlined in Section 16.3.1. The addition of organic matter into the sediment samples should be avoided.

16.4.5.1 Equipment

- Site maps indicating the locations of samples, sample analysis request forms
- Specialized Sampling Devices (used in atypical situations): boat for sampling ponds, lakes, and rivers, if warranted, Stainless steel pitcher (clamped to a telescoping aluminum pole when necessary), Sediment dredge, such as a Ponar sampler, for deep sediment samples, Decontaminated stainless steel bowls and spoons
- Reagents for sample preservation, if sample containers not pre-preserved by the laboratory
- Sample bottles and sample labels
- FID or PID (e.g., OVM), if warranted
- QA/QC: Trip blanks and extra sample sets for collection of field blanks, duplicates
- MS/MSDs, MRD duplicates, and any other QA/QC samples
- Coolers packed with enough ice and/or cold packs to maintain sample preservation
- Sample Record forms and Chain-of-Custody forms
- Field log book, surface water sampling record form (Appendix C)
- Indelible ink markers, pens
- Pocket calculator, wristwatch/time
- Marker flags or stakes
- Paper towels and trash bags
- Clean plastic sheeting and 5-gallon buckets
- PPE: vinyl, neoprene, and/or nitrile gloves, Tyvek, Hip waders and/or waterproof boots, Level C equipment if necessary
- Deionized/Distilled water, paper towels, and trash bags
- Folding ruler

- Decontamination supplies and reagents: Alconox (or equivalent), gloves (latex, nitrile, or scrub brushes equivalent), brushes

- Field instrumentation for on-site measurements (e.g., pH, conductivity, dissolved oxygen, oxidation reduction potential, turbidity meters, volatile organic compound monitor), and
- Health and safety equipment as described in the site-specific Health and Safety Plan

16.4.5.2 Field Procedures

The process for collecting sediment samples is as follows:

1. A new pair of clean disposable latex or nitrile gloves will be donned at each sampling location.

2. In shallow streams and ditches that allow wading, sediment samples will be collected by using a decontaminated stainless steel spoon or scoop. In areas where wading is not possible, a hand auger or scoop attached to a pole may be needed to collect sediment samples.

3. While facing upstream, collect the sample by scooping along the bottom of the surface water body. Remove excess water and place the sediment sample into a decontaminated stainless steel bowl.

4. After a sufficient sample volume has been collected into the stainless steel bowl, the sample will be homogenized using the quartering method and then placed into the appropriate sample bottle. If volatile organic analysis samples are required at the site, these shall be collected first, prior to any mixing of the sediment. The rest of the samples will be collected after the remaining sediments in the bowl have been stirred for homogenization purposes.

5. After the sample bottle is filled, the cap will be placed on the bottle and the sediment samples will be stored in an ice-filled cooler immediately after sampling is complete. The samples will be packaged for shipment as specified in Section 5.3.

6. QA/QC samples will be collected as specified in the SS-WP.

16.4.6 Soil Gas Sampling

This section presents the general information on soil gas sampling. If soil gas sampling is warranted for specific site, detailed SOPs will be presented in the SS-WP.

Soil gas may be sampled using commercially available soil gas sampling probes, a gas tight syringe or bulb, a SUMMA® canister, sorbent tubes, or a Tedlar® bag.

When soil gas samples are collected using commercially available soil gas sampling probes, the probes are connected to a steel drive shaft used to push the probe to the desired sampling depth. The sampling container shall be a glass or metal bulb equipped with an entrance and exit spigot. The Tygon® or Teflon® tubing (as specified in the SS-WP) from the sampling probe shall be attached to the entrance spigot, and a second length of tubing shall run from the exit spigot of the bulb to a portable vacuum pump. At each sample location, the sampling probes shall be driven to a previously determined depth of between 5 to 10 feet below ground surface. When the probe is at the desired depth, the steel drive shaft shall be pulled back slightly, exposing the gas intakes on the sample probe. The vacuum pump shall then be switched on, drawing the gas contained in the interstitial spaces of the soil through the probe, tubing, and sample container. The purge volume should be equal to the sum of the volumes of the tubing and the space below the drive rod when the rod is pulled up. For example, with 10 feet of 1/8-inch tubing and a 1-inch space below the drive rod, approximately 42 mL would need to be purged. This can easily be done with a 60 mL syringe and a stainless steel three-way valve. After the appropriate purge volume of gas have been drawn, the Tygon® or Teflon® tubing shall be clamped shut on the downstream side of the bulb (toward the pump) and then the upstream side of the bulb. The vacuum pump shall then be switched off. The volume of 2 liters shall ensure that the gas in the glass bulb originated from the soil interstitial space, rather than the tubing, so long as a reasonably short tubing length is used. Following sample collection, the sample container shall be labeled and the sample number recorded in the field log book along with the following information: soil gas sample or probe depth, apparent moisture content (dry, moist, saturated) of the sampled zone, if available, soil gas purge rate, sampling duration, sampling system leak rate, and pump vacuum, description of sample containers, location of sample analysis, location and grid layout of sampling stations.

Gas tight syringe or bulb samples are collected for on-site laboratory analyses. To collect a syringe sample, a fitting with a Teflon® septum shall be installed in the sampling line ahead of the purge pump. After purging the required volume, samples are collected. Bulb samples are collected using a manifold configuration.

SUMMA® Canister samples are collected for off-site laboratory analyses. A fitting for attaching the canister shall be installed in the sampling line ahead of the purge pump. Prior to sampling, the initial canister vacuum is measured, the canister is attached to the sample line, and the probe, etc. is purged. The canister sample is then collected.

Sorbent tubes may be used to collect samples for real-time field analysis (i.e., colorimetric tubes such as Draeger tubes) or for off-site laboratory analyses. The well or probe is purged, the sorbent tube is installed in the sampling line, and the required volume of soil gas is drawn through the tube. Colorimetric tubes are read directly, while sorbent tubes are capped and stored on ice (dry ice may be required) until being shipped to the laboratory.

Tedlar® bag samples can be collected for field analysis using real-time instruments or for off-site laboratory analysis. An oiless diaphragm pump is attached to the sampling line and a Tedlar® bag is attached to the pump exhaust. Samples shall be kept out of direct light and analyzed within 24 hours of collection to minimize the potential for loss, reaction, or degradation of VOCs. If Tedlar® bags are used, a blank bag sample should also be collected for each lot of bags used. The blank bag sample should be filled with pure nitrogen and submitted as a field blank. Cautions should be exercised when using Tedlar® bags as they can contain trace amounts of compounds, particularly petroleum hydrocarbons.

No matter what methods will be used to collect soil gas samples, cautions need to be exercised to prevent ambient air intrusion into the sample. Different measures shall be taken based on the specific project objective. All samples for inclusion in a risk assessment should include the following steps to prevent ambient air intrusion:

- Packing a hydrated bentonite seal around the probe at the ground surface;
- Conducting a leak test to make sure there are no leaks in the sampling train. Use a syringe to pull a vacuum prior to pulling up on the drive rod. If the vacuum is present, there are no leaks;
- Limiting the purge and sampling rate to no more than 200 mL per minute. In addition to increasing the chance for ambient air infiltration, higher rates can cause biased high concentrations by "stripping" contaminants adsorbed to soil particles. It is recommended that all purging (and sampling for Tedlar Bags) be done with a syringe to minimize the purge rate. The sampling rate should be similar to the purge rate. Flow regulators may be required to limit the sampling rate of summa canisters;
- It is recommended that a tracer compound be used to test for ambient air intrusion. The draft New York State Department of Health guidance (Guidance for Evaluating Soil Vapor Intrusion in the State of New York, Public Comment Draft, February 2005), recommends using a gas, such as helium or butane as a tracer. Another easier method is to use rubbing alcohol (2-propanol). Paper towels can be soaked with 2-propanol and place around the base of the drive rod, around the tubing where it exits the drive rod, and at any other connections or fittings. The 2-propanol will volatilize and will be detected in the sample at a high concentration if ambient air infiltration is significant.

In addition to the information listed in Section 16.6, the following information shall be recorded. If only qualitative data are required, only items 1 and 6 are needed: (1) soil gas sample or probe depth, (2) apparent moisture content (dry, moist, saturated) of the sampled zone, (3) soil gas purge rate, sampling duration, sampling system leak rate, and pump vacuum, (4) description of sample containers (if any), (5) location of sample analysis, (6) location and grid layout of sampling stations, (7) instrument calibration.

16.4.7 Composite Sampling

Occasionally, samples will be composited prior to chemical or physical characterization. Composites will be collected in the following steps:

- Discrete subsamples of equivalent size (weight, volume) will be collected from each of the selected locations and combined in a common receptacle;
- All necessary sample preparative operations (e.g., sample filtration, sleeve screening) will be performed on the subsamples in the receptacle;
- The material remaining after preparation will then be fully homogenized, generally by mixing;
- Any necessary preservatives will be added;
- The required samples will be collected and placed into clean sample bottles and packaged for shipment;
- Samples collected for certain types of analyses (volatile organic compounds and sulfides) WILL NOT be composited unless compositing is specifically requested by a regulatory agency.

16.4.8 Confirmatory Sampling

Confirmatory soil sampling will be conducted at each site where excavations or removal of piles or berm structures are performed. The goal of the confirmatory sampling is to provide data that verifies that the identified contamination has been removed, and that concentrations of contaminants remaining at the subject site comply with documented cleanup objectives established by the Army. If the results obtained from the analysis of confirmatory soil samples verify that the Army's cleanup objectives have been obtained, no further excavation will be conducted at the subject site. If the analytical results for the confirmatory samples do not verify that the Army's cleanup objectives have been obtained, further excavation will be conducted until such verification is provided.

16.4.8.1 Equipment

- Field Book and Project Plans
- Sample Labels
- Shipping Labels
- Sample Records
- Shipping Forms
- Chain-of-Custody Forms

- Camera
- Photo-ionization Detector
- Personal Protective Equipment in accordance with the Health and Safety Plan
- Marker stakes, flagging and paint
- Tape Measures
- Decontamination Supplies
- Inert (e.g., stainless steel or Teflon®) sampling equipment
- Hand Auger
- Mixing Bowls
- Pre-cleaned Sample Bottles
- Plastic Sheeting
- Shipping Tape
- Ice Chests and Ice (for sample transport)

16.4.8.2 Number, Frequency, and Location of Confirmatory Sampling

Number, frequency, and location of confirmatory samples will be specified in the SS-WP. This section provides some general requirement for confirmatory sampling.

Confirmatory soil samples will be collected from the base and sidewalls of each excavation, except in the circumstance where the depth of the excavation measures 12 inches or less. In situations where the sidewalls of an excavation are 12 inches or less in depth, sidewall samples will not be collected, but will be replaced by confirmatory samples that are collected outside the perimeter of the excavation. Confirmatory samples will also be collected from locations beneath and around every aboveground soil pile or berm structure that is removed.

At least one discrete sample will be collected from each face of an open excavation that is 12 inches in depth or greater. Thus, a minimum of five confirmatory samples (i.e., one base, and four sidewall samples) will be collected at each excavation. Additional confirmatory samples will be collected at a rate of one per every 2,500 square feet of surface area, or fraction thereof, found on an exposed excavation face.

For excavations where the depth of the excavation is less than or equal to one foot below grade, confirmatory samples will be collected from the perimeter of the excavation at a rate of no less than one sample per every 100 linear feet of length on each edge of the excavation. A minimum of one sample will be collected along each edge of the excavation. Additionally, at least one sample will be collected from the base of the excavation, and additional samples will be collected from the base of the excavation at a rate of one per every additional 2,500 square feet or less of surface area.

For aboveground soil piles or berm structures that are removed, at least one sample will be collected from a point that is directly beneath each pile or berm structure, and from at least four other locations (e.g., major compass point locations) that are located around the perimeter of the pile or berm. Additional samples from beneath the pile will be collected at a rate of not less that one per every 2,500 square feet or less of surface area underlying the pile or berm, and at a rate of at least one per every 100 linear feet of the piles or berms perimeter.

Locations of confirmatory sampling will be biased towards areas that are most likely to be contaminated. Visual and olfactory sensing and use of portable field monitoring devices (e.g., photo-ionization detectors) should be used, within the bounds of the site-specific health and safety plan and good operating procedures, to assist in the selection of confirmatory sampling locations.

Additional confirmatory samples should be collected an analyzed, as may be needed, based on results of field screening and observations, or based on professional judgment.

16.4.8.3 Field Procedures

1. Once the excavation is complete, a drawing of the completed excavation will be prepared and necessary measurements shall be recorded in the field notes. Specific measurements collected will include the length, width, and depth (if subsurface excavation) of the excavation. The depth of the excavation will be reported at each corner, and at intermediate locations that are no further than 100 feet apart. These measurements will be used to document that sufficient samples have been collected from the excavation to reasonably assess whether residual contamination remains in the area of the excavation.

2. Once the drawing of the excavation is prepared, all proposed sampling locations will be marked and labeled and information describing the location of each proposed sampling location will be transcribed into the field notes and onto site maps. Each sampling location must be uniquely identified with a sample location.

3. Confirmatory samples will be collected from a depth of not less than one-inch below the excavation's surface and not more than six inches below the excavation‘s surface. The one-inch minimum is recommended to ensure that soils exposed directly to the atmosphere, which could result in the off-gassing of volatile organic or inorganic (e.g., sulfide or cyanide) compounds and a decreased level of volatile content over time, are not collected and used for the volatile compound analyses. The depth from which confirmatory samples are obtained will be recorded in the field notes at the time of collection.

4. At the time of their collection, confirmatory soil samples will be visually described for:

a. Soil type,

b. Color,

c. Moisture content,

d. Texture,

e. Grain size and shape,

f. Consistency,

g. Visible evidence of staining or discoloration, and

h. Any other observations (e.g., odors).

5. All data collected at the time of sample collection will be transcribed into the field records. The identity of the sampler, the date and time of sample collection, the location of the sample collection (i.e., location id), the identity of the sample (i.e., sample number), a description of the sampling method (e.g., auger, trowel, spade, homogenized, etc.) used, the number of sample containers collected, and the intended analysis that will be completed will be recorded.

6. All sampling will be completed using decontaminated, inert (e.g., stainless steel, Teflon®, etc.) sampling equipment. Selected sampling equipment may be used for all collection activities conducted at one location (e.g., the sample and its duplicate for all required analyses) during one contiguous time period; however, once the equipment has been used at one location, it can not be used at another location until it has been thoroughly decontaminated per prescribed procedures.

7. Samples collected for volatile compound analyses (e.g., volatile organic compounds or cyanide) will be collected first and will be transferred directly from the ground to the appropriate sample container (e.g., EnCore™). Samples for volatile compound analyses will not be homogenized. Samples collected for non-volatile analyses (e.g., semivolatile organic compounds, pesticides, metals, nitrate, total organic carbon (TOC), total petroleum hydrocarbon (TPH)) should be collected and transferred to an inert mixing bowl and homogenized prior to being placed into their final sample bottles.

8. A recommended order for sample collection is provided below:

Collected without homogenization

Volatile Organic Compound

Volatile Inorganic Compounds (cyanide, sulfide, nitrite, etc.)

Collected, homogenized, and split into required bottles

Semivolatile Organic Compounds

Pesticides/PCBs

Herbicides

Explosives

Total Petroleum Hydrocarbons

Total Organic Carbon

Metals

Anionic Species (Chloride, Sulfate, Nitrate, etc.)

16.4.9 Air Sampling

This section presents methods of collecting air samples for metal analysis and SVOC analysis. All other air sampling programs, if warranted for specific site, shall be specified with detailed SOPs in the SS-WP.

Metals

This section covers three methods to collect air samples for metals - one for gaseous phase mercury, one for lead in airborne particulate, and the third for all other target metals in airborne particulate. All other analyses, if warranted, will be presented in the SS-WP.

Air samples for gaseous phase mercury will be obtained using National Institute for Occupational Safety and Health (NIOSH) Method 6009, which employs the use of a personal sampling pump to draw sample air through a glass sorbent tube. Sample air is drawn through the tube at a constant known flow rate between 0.15 to 0.25 liters per minute for a total sample size between 2 and 100 liters. The exposed tubes

were then sealed and sent to an environmental analytical laboratory for mercury analysis. A copy of the method is attached in Appendix F.

Air samples for airborne particulate phase lead will be collected using NIOSH Method 7082, which employs the use of a personal sampling pump to draw sample air through a cellulose easter filter (0.8µm). Sample air is drawn through the filter at a constant known flow rate between 1 and 4 L/min for up to 8 hours for a total sample size of 2000 to 1500 liters for time-weighted average measurements. The exposed filter were then sealed and sent to an environmental analytical laboratory for analysis for lead. A copy of the method is attached in Appendix F.

Air samples for all other target metals will be obtained by the USEPA reference method for determination of the particulate matter less than 10µm aerodynamic diameter (PM_{10}) concentrations in air, as published in 67 Fed. Reg.,15566, April 2, 2002. This standard high-volume particulate sampling method RFPS–0202–141, titled ‘‘Tisch Environmental Model TE–6070 PM10 High-Volume Air Sampler,’’ consists of a TE–6070 PM10 size selective inlet, 8″ x 10″ filter holder, aluminum outdoor shelter, mass flow controller or volumetric flow controller with brush or brushless motor, seven day mechanical off/on-elapsed timer or 11 day digital off/on-elapsed timer, and any of the high volume sampler variants identified as TE– 6070–BL, TE–6070D, TE–6070D–BL, TE– 6070V, TE–6070V–BL, TE–6070–DV, or TE– 6070DV–BL, with or without the optional stainless steel filter media holder/filter cartridge or continuous flow/pressure recorder. An operations manual is attached in Appendix G. Metal concentrations in air can be derived by multiplying metal concentration in PM_{10} and PM_{10} concentration in air with appropriate unit conversion.

Semivolatile Organic Compounds

Air samples for SVOCs will be obtained by using Method TO-13 (USEPA, 1999), which utilizes a modified high-volume sampler in conjunction with a particulate filter and a combination of XAD-2 resin and polyurethane foam (PUF) adsorbent in a glass cartridge. The low level of SVOCs in the air requires the use of a relatively high-volume sampling technique to acquire sufficient sample for analysis.

The sample collection media for SVOCs consisted of a filter (for particulate phase SVOCs) followed by an adsorbent glass cartridge filled with PUF/XAD/PUF (for gaseous phase SVOCs).

16.4.10 Wipe Sampling

This section presents protocols for wipe sampling that may be necessary within buildings. This section presents the wipe sampling SOP that can be used to collect wall, roof, and other surface samples.

16.4.10.1 Equipment

- Field Book and Project Plans
- Sample Labels
- Shipping Labels
- Sample Records
- Shipping Forms
- Chain-of-Custody Forms
- Camera
- Indelible ink markers, pens
- Personal Protective Equipment in accordance with the Health and Safety Plan
- Marker stakes, flagging and paint, yellow ribbon
- Tape Measures
- Decontamination Supplies, Alconox (or equivalent), brushes
- Gloves (latex, nitrile, or scrub brushes equivalent),
- 3-inch by 3-inch cotton gauze pads presoaked with appropriate solvent (as specified in the SS-WP)
- Decontaminated pair of tweezers or forceps
- Decontaminated wipe template
- Pre-cleaned sample bottles (Teflon®, stainless steel, or glass)
- Plastic sheeting and paper towels
- Shipping tape and clear tape
- Trash bag, storage container for contaminated sampling equipment
- Ice Chests and Ice (for sample transport)

16.4.10.2 Field Procedures

1. Assemble all equipment necessary for wipe sample collection prior to leaving the office.

2. Identify and mark and exclusion zone with yellow ribbon to keep unauthorized personnel from entering the area where the work will be performed.

3. Identify and mark an external limited access zone where sampling equipment can be placed, once it has been used, pending decontamination and recycle. If field decontamination of sampling equipment is a planned event, necessary decontamination reagents and supplies should be placed in this area prior to sample collection. If field decontamination is not planned, used sampling equipment should be placed into a polyethylene bag and a transport container after it is used.

4. Identify and record specific descriptive details for one or more locations that will be used as reference points for positioning all wipe samples. Suitable locations may include lower right hand

corner of an entry doorway, the northeastern corner of the enclosure or pad. Photograph each reference point, and record sufficient pertinent information within field sampling documentation that will allow future reviewers to recreate the sampling event.

5. Locate the approximate area of the proposed sampling points using a tape measure and facility map. Mask off an area that is larger than the proposed sampling area (10 centimeters (cm) by 10 cm – 100 cm^2) and annotate the sample site identification on a piece of tape that is placed outside of the area to be sampled. Photograph each sampling location and the overall sampling grid and record details of the site within the field documentation.

6. Don protective gloves and prepare needed 3-inch by 3-inch cotton gauze pads. The gauze pad should only be touched using a decontaminated pair of tweezers or forceps. Do not touch the gauze with bare or gloved hands as dirt and oils from your skin or the surface of the gloves may contaminate the samples. Similarly, do not let the gauze pad touch any surfaces that may be contaminated. Place the gauze pad in a clean, resealable sample vial. The sample vial should be constructed of inert materials (i.e., Teflon®, stainless steel, or glass) and contain no materials (e.g., waxed sealing lids) that could contaminate the sample.

7. Soak each needed 3-inch by 3-inch cotton gauze pads with 15 to 20 milliliters each of an appropriate solvent (as designated in the SS-WP). Reseal the sample vial and place in a secure stand or container pending use.

8. Assemble all equipment needed for the collection of a wipe sample at one location and move it to the first sampling location.

9. Don a new pair of disposable gloves. Use a respirator equipped with an organic vapor cartridge if the sample collection and preparation will be completed in an area that is not well ventilated.

10. Inspect the area to be wiped and select a location where the wipe template will be placed. Place and tape an inert, decontaminated, wipe template over the selected sampling site. The tape must be kept exterior to the surface that will be wiped. Adhesive from the tape should not contact the surface within the wiping area as it may contaminate the sample. Do not touch the surface to be wiped with gloved hands. Tape and gloving materials can be a significant source of organic compounds such as phthalates which will contaminate the samples.

11. Open the sealed sample vial containing the pre-soaked gauze pad, and remove the pad using a decontaminated pair of forceps. All subsequent wiping motions should be done in a manner that ensures that all chemical materials recovered from the surface are concentrated on one side of the gauze.

12. Collect the sample by applying uniform pressure to the wipe pad as it is drawn with straight, even strokes, over the area to be wiped. Successive strokes used should overlap slightly to ensure that the entire are is wiped. The first sequence of strokes should be conducted from left to right, moving from the top of the sampling square to the bottom of the sampling square.

13. Once the first sequence of wiping repetitions is completed, the entire square must be wiped a second time with the same pad in a direction that is perpendicular to the first wiping pattern. Therefore, start at the upper left hand corner of the sampling square and wipe moving towards the right. Start each subsequent pass at the left side of the sampling template at a location below but overlapping the previous pass and move successively to the right and down until the entire square is wiped a second time.

14. Let the gauze air dry.

15. Fold the dry gauze so the sampling side is inwards and place it in the pre-cleaned sample vial using the forceps. Again, gloved hands and tape should not be allowed to contact the gauze as they will contaminate the sample.

16. Inspect the area just wiped. If the surface still appears to contain residue, use additional pre-soaked gauze pads to complete additional repetitions of steps 11 through 15, above. Each selected surface must be wiped until no residue is observed to remain at the site. Each successive gauze pad should be used for only one vertical and horizontal wiping sequence as is described above. Place all additional gauze pads used at one sampling location in the same initial sampling vial.

17. Cap the sample vial containing the used gauze pads.

18. Label the sample vial with a unique sample code, information on the sampling site, the date/time of collection and the personnel responsible for the sample collection.

19. Place the sample vial in an ice chest that is packed with ice. A sample temperature of 4°C ± 2°C must be achieved and maintained during storage.

20. Remove the template and the tape from the surface and remove all tape. Place tape in a trash bag that will subsequently be designated for appropriate disposal. Place all used sampling equipment in a container that will be used to transport it to the point of decontamination.

21. Remove and discard gloves in the trash bag.

22. Label the sample vial and document the sample collection process in the field book.

23. Decontaminate all sampling equipment before reuse at another site. All sampling equipment should be decontaminated using pesticide grade hexane. Let equipment air dry and wrap securely in clean aluminum foil pending use at another site.

24. Complete chain-of-custody forms and pack samples for shipment to the laboratory. The samples should be pack on ice and maintained at 4°C ± 2°C until delivered to the laboratory.

16.4.10.3 Quality Assurance and Quality Control Samples

Field/Ambient Blank – Prepare gauze with solvent as described in procedure above, but do not use to wipe a surface. Allow to air dry, fold, and place in sample vial. Label, record collection details in field book and enter on chain of custody. Ship to laboratory for analysis.

Duplicate – Wipe two adjacent areas at the same sampling location following procedures defined above. Separate equipment must be used. The sample and duplicate pair should be collected from areas that appear to be identical. During sample collection operations, ensure that the sampling activities completed for the first sample do not contaminate the area designated for the collection of the duplicate. Ensure that tape and discarded materials do not impact the adjacent sites.

Trip Blank – To be collected for all media. Trip blank to be supplied by the analytical laboratory and be shipped to and returned to the laboratory with the sampling equipment.

One sample duplicate and a field blank must be collected for each SDG of 20 field samples or less. A trip blank should accompany each shipment of field samples sent to the laboratory. All sampling equipment and samples should be stored and packaged in an equivalent manner during their time in the field.

16.4.10.4 RINSATE SAMPLE COLLECTION PROTOCOL

This procedure is to be used to obtain representative samples for analysis from concrete floors, secondary containment areas and sumps, including surfaces that have been coated, to establish whether or not there is any contamination on the concrete surfaces. This procedure is to be performed after the surfaces have been cleaned and decontaminated, usually pursuant to the approved Closure Plan[1]. This procedure may also be suitable for use on other surfaces on a case-by-case basis.

[1] A detailed washing and rinsing (i.e., decontamination) procedure, as approved by the regulators, will be followed based upon the selected technology. USEPA (1985) Guide for Decontaminating Buildings, Structures, and Equipment at Superfund Sites or its most recent update can be used to develop such technology.

1. Create an exclusion zone with colored (e.g., yellow) ribbon to keep extraneous personnel from entering area.

2. Sketch the area to be sampled. Sketches should include locations of building columns, walls, fixed equipment, and the proposed rinsate sampling locations themselves (to accurately locate the rinsate sampling points within the buildings) for Department concurrence. The sample locations must be chosen to include any areas of staining, discoloration or other evidence of spills. The sample locations will be approved by a NYSDEC staff person usually onsite on the day of sampling (unless NYSDEC chooses not to be present or states that such approval is not needed). Each sample location should be approximately 2500cm^2 (say 50cm by 50cm) or 400in^2 (say 20in by 20 in), but size may be adjusted to the extent necessary to accommodate field conditions with NYSDEC approval.

3. Assemble and clean all equipment necessary for sample collection. Equipment needs to be cleaned, if not already pre-cleaned by the laboratory.

4. Create a temporary containment area on the storage zone floor using an inert, clean or cleaned, flexible boom (e.g., water filled polyethylene tube, nonabsorbent spill containment berm), if necessary. If the floor is relatively level and water will puddle without flowing out of the sample location, a boom may not be not necessary.

5. Label the sample containers with a unique sample code, information on the site, sample locations and the date and time samples were collected. Affix appropriate labels for test parameters on the sample containers. Put on a new pair of disposable nitrile gloves.

6. De-ionized water is to be used for this protocol. The de-ionized water may be provided by the laboratory. For each sampling location, start with two liters or 2 quarts of de-ionized water to allow for the collection of a sufficient sample size for all of parameters to be tested for, as specified by the laboratory, including QC samples. If necessary, additional de-ionized water may be used, but no more than the minimum amount needed to provide a sufficient sample size. Record the temperature of the room and of the de-ionized water. At each sampling location, slowly pour the de-ionized water onto the surface to be sampled. A clean/cleaned wash bottle may be utilized to cover the area uniformly with the de-ionized water. If the individual area is sloped, start pouring at the highest elevation. Record the volume of de-ionized water used for each sample location.

7. Allow de-ionized water to collect and remain in the sample location for 10 minutes.

8. For each sampling location, collect the number and type of samples as specified in the closure plan along with appropriate QA/QC samples. Samples shall be collected using dedicated, sterile glass pipettes provided by the laboratory. The pipettes will be used to transfer the sample fluids into the

appropriate bottles provided by the laboratory. Volatile sample bottles shall be filled first to minimize loss of volatiles. Record the volume of water collected for each sample for each sample location.

9. Samples must not be composited.

10. Cap the sample containers and place them in a laboratory cooler with ice to maintain a temperature of 4 ^{o}C.

11. Measure the exact wetted area for each sampling location sampled using a tape measure or other suitable device. Place all measurements and the sketch of the area in the site field book. Measurements should include all appropriate or unusual conditions observed while collecting each sample (i.e., drainage patterns followed, stained areas present, condition of storage zone floor, etc.).

12. Remove and discard the gloves. Place all disposable gloves into a plastic bag designated for proper disposal.

13. Enter information on procedures followed including details of samples and sampling in the field book. Photographs of the sample locations, wetted areas, equipment, and actual sampling events may be taken by the facility or Department staff and a list of the photographs shall be recorded in the field book.

14. Fill out chain-of-custody forms. Prepare the samples for storage and shipping in laboratory cooler with sufficient ice to maintain a temperature of 4 ^{o}C. Ship overnight to the laboratory for analysis.

15. Follow chain-of custody procedures as detailed in the Quality Assurance Program Plan.

16. Analytical Methods

All of the samples need to be analyzed by a laboratory certified by NYSDOH ELAP for the parameters of interest. The following preparation and analytical methods may be used.

PARAMETER	**PREPARATION***	**ANALYSIS**
TCL Volatiles	Method 5030	Method 8260
TCL Semi- Volatiles	Method 3640	Method 8270
Pesticides	Method 3620	Method 8081
TAL Metals	Method 3010/3015/3020 as appropriate	Method 6010 and 7000 series as appropriate

* Preparation Methods should be used where appropriate, prior to analysis

17. Target Detection Limits and QA/QC

    The target detection limits for TCL volatiles and TCL semi-volatiles is 5ug/L. The target detection limits for the metals is as per the table from the NYSDEC ASP.

    The quality control results shall be submitted along with the sample results. This QC data shall include surrogate recoveries, MS/MSD percent recoveries, internal standard area counts and retention times (as applicable), and blank results for the organics. For the metals, submit CRQL standard for Atomic Absorption (AA) and ICP, spike sample recovery, duplicates, blanks, ICP interference check sample, post digestion spike sample recoveries (if applicable), laboratory control sample results, and ICP serial dilution results. The QC analysis should be performed on site specific samples. The QA/QC requirements of SW-846 shall be met.

18. Clean closure criteria

    The sample results for the rinsate samples shall be compared to the New York State Water Quality Standards for Class GA groundwater, 6 NYCRR Part 703.5 which are available at www.dec.state.ny.us/website/regs/703.htm.

16.4.11 Radiological Surveys

This section presents general information for several common types of radiological surveys that may be required at SEDA. Surveys may be required during the remedial process to determine that all suspected radioactive contamination in an area, if present, has been removed, and to assess and minimize worker exposure if a radiological hazard is present. All field personnel performing radiological surveys should receive a minimum 1-hour of radiological safety and fundamental training, as well as a minimum of 24 hours of onsite orientation and technique training. This will include a briefing on the potential risks associated with radiological contaminants. All radiation survey work onsite will be overseen by a HP/RSO. All work will be conducted in accordance with the Generic Site-Wide Health and Safety Plan for Seneca Army Depot Activity (Parsons, 2005). Site-specific sampling and measurement plans, DQOs, and site release criteria will be developed as necessary using the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM; USEPA, USNRC, USDoE, USDoD, 2001), instrument and survey-specific SOPs, and other applicable federal and state guidance.

16.4.11.1 Gamma Radiation Surveys

Surveys for gamma radiation are commonly performed with sodium iodide (NaI) based scintillation detectors. General surveys, and surveys for higher energy radionuclides, are performed with detectors with larger (e.g., 2” by 2”) crystals, while surveys for lower energy gamma radiation and x-rays may be performed using smaller crystals, such as the crystal in a FIDLER detector. Gamma radiation may be

measured in units of counts per minute (cpm), and in some cases measurements may be correlated with a soil or volumetric concentration in units of picocuries per gram (pCi/g). In addition, some gamma instruments report an exposure rate, which can be used to monitor worker exposure.

16.4.11.2 Alpha and Beta Radiation Surveys

A variety of instruments are available to perform surveys for alpha and/or beta radiation, including gas proportional detectors, plastic scintillators (e.g., phoswich detectors), and Geiger-Mueller (GM) detectors. Due to the short range of alpha radiation, alpha surveys are typically only performed on flat, smooth surfaces. Alpha and beta radiation may be measured in units of cpm and converted to a surface activity concentration of decays per minute per 100 square centimeters (dpm/100cm^2).

16.4.11.3 General Radiation Survey Procedure

The following is a general operating procedure for the use of radiation detection instrumentation for field surveys. Instrument and survey-specific procedures will be included as necessary for site-specific SAPs. Site-specific sampling requirements, such as the required number of measurements and minimum detectable activities, will be determined using MARSSIM and other appropriate guidance.

1. Prior to use, the survey instrument should be calibrated to NIST and other applicable standards by a qualified vendor or manufacturer. The calibration should account for the specific radionuclides of concern at the site, and for any unusual field conditions to be encountered. Calibration of instruments should take place a minimum of once per year.

2. Conduct instrument function checks at a minimum of twice per day – prior to the collection of data, and after the collection of data. Function checks should also be performed if the instrument is damaged, anomalous measurements are suspected, or if batteries are changed. The function checks should include a battery check, a visual inspection for damage, a check of the high voltage setting, a background measurement, and a source measurement with a check source of appropriate type (e.g., Cs-137 for gamma radiation, Th-230 for alpha radiation, or Tc-99 for beta radiation). The manufacturer's operating manual for the instrument should be consulted during this process. Background and source function check measurements will be logged and entered into a control chart to monitor the performance of the instrument. If the instrument demonstrates repeatable and unexplainable anomalous function check measurements, it will be removed from service, and data collected with that instrument will be evaluated to determine its usability.

3. Prior to conducting surveys at the impacted area, an appropriate background or reference area should be located. Background surveys should include measurements of the different types of materials expected at the impacted area. An instrument flag value will be developed using the background data and other appropriate action levels.

4. For background and impacted area surveys, proper scanning techniques should be observed. The appropriate scanning procedures are dependant on the radionuclides of concern, the instrument being used, and the desired detection limits. Field scanning techniques for different types of surveys will be included in SOPs for specific site investigations, personnel will be trained in these techniques prior to the start of the field surveys. The SOPs and training will include information on appropriate scanning speed, distance from detector to surface, required use of audio, and other appropriate topics.

5. Collected data will be evaluated on a daily basis by a health physicist or other qualified individual. Errors or concerns will be addressed as soon as possible, while still in the field. After the field survey is complete, the data will be analyzed in accordance with MARSSIM and other applicable guidance.

16.4.12 Filtering Groundwater or Surface Water Samples

Filtered groundwater or surface water samples can only be collected after approval from the project manager. This section provides the procedures for filtering groundwater or surface water samples for dissolved metal analysis. The procedures were modified from the SOP 2200 series developed by Florida DEP (2004).

1. Unless specified by the SS-WP, use a 1 micrometer (µm) filter.

    1.1 Use a disposable, high capacity, 1 µm in-line filter.

        1.1.1 Flush the filter with 30-50 mL of analyte free water or an inert gas (nitrogen) to remove atmospheric oxygen;

        or

        1.1.2 Insert the filter on the high pressure side (i.e., on the delivery side) of the pump. Hold the filter upright with the inlet and outlet vertical. Pump water from the aquifer through the filter until all atmospheric oxygen has been removed.

    1.2 Use a variable speed pump that can be fitted with an in-line filter on the outlet end. Peristaltic pumps, bladder pumps or submersible pumps can be used when water levels are no greater than 20 to 25 feet deep; bladder pumps or submersible pumps must be used when water levels are greater than 20 to 25 feet deep.

        1.2.1 Install new or precleaned silastic tubing in the variable speed peristaltic pump head at each monitoring well.

1.2.2 Use new or precleaned delivery tubing at each monitoring well.

1.3 Collect filtered samples by either of the methods outlined below if the static water level in the well is too deep for a variable speed peristaltic pump and a variable speed electric submersible pump or variable speed bladder pump of appropriate configuration is not available. Do not agitate the sample or expose it to atmospheric oxygen. **Do not** pour the sample into any intermediate vessel for subsequent filtration.

1.3.1 Collect the sample in a Polyethylene, Teflon® or positive pressure bailer that can be pressurized. When the bailer has been retrieved, immediately connect the filter and begin to pressurize the bailer;

or

1.3.2 Collect the sample with a bailer and immediately place the intake tube of the peristaltic pump into the full bailer and begin pumping the water through the filter as described in section 1.2 above.

1.4 Do not use the following equipment for filtering groundwater samples for metals:

1.4.1 Any pump and apparatus combination in which the filter is on the vacuum (suction) side of the pump.

1.4.2 Any type of syringe or barrel filtration apparatus.

1.4.3 Any filter that is not encased in a one-piece, molded unit.

16.4.13 Core Sample Collection

Core samples should be collected following the appropriate SOP to ensure that core samples are representative of the surfaces that they are intended to characterize. This section presents the SOP for concrete core sampling. This SOP was revised from an SOP originally established for PCB analysis. The SOP should be reviewed carefully before being applied for other analysis. Other concrete sampling methods such as the USEPA Region 1 (1997) Draft SOP for Sampling Concrete in the Field (as attached in Appendix F) can be selected for specific project if deemed appropriate.

16.4.13.1 Sampling Preparation

Prior to arriving at the site, the designated Field Team Leader is responsible for completing the following procedures:

1. Obtain proper sampling equipment as listed in Table 25.
2. Obtain a sufficient number of food-grade Ziploc® bags (1-gallon) and appropriate Chain-of-Custody records, custody seals and other supplies. Verify that the analytical laboratory has been contacted and is prepared to receive the samples.
3. Review the SS-WP, the appropriate sampling procedures, the Generic Site-Wide Health and Safety Plan for Seneca Army Depot Activity (Parsons, 2005), and this SAP. Discuss with the Project Manager to establish specific sampling requirements. The SS-WP and SAP and associated appendices must be on-site through task completion for reference by field personnel.
4. Make arrangements with on-site personnel for obtaining site access.

16.4.13.2 Decontamination

Once at the site, the Field Team Leader is responsible for setting up the decontamination area and decontaminating any non-disposable sampling equipment (i.e., coring bits). The coring bits shall be thoroughly cleaned before initial sample collection, between collection of each subsequent sample, and prior to taking the equipment off-site. Decontamination SOP is presented in Section 16.3.11.1.

16.4.13.3 Core Sample Collection

The locations for core sampling shall be clearly marked in the field logbook with the appropriate sample location code. The following steps will be followed to collect core samples from building wall surfaces:

1. Evaluate overhead conditions (e.g., window glass, loose timber, bricks, etc.), and inspect walls for damage, loose debris, or potentially hidden items/conduit prior to coring. Any visual indications of unsafe or unsuitable conditions shall be handled by relocating the core sampling to a different area on the wall.

2. Select the area to be sampled.

3. Install a 2-inch diameter core into the surface using a horizontal portable coring drill. Unless specified by the SS-WP, wall cores will be collected continuously through the full thickness of the wall.

4. Cool the coring bit during coring procedures using distilled water.

5. Collect the cooling water using a wet vacuum and store the water in a 55-gallon DOT-approved drum.

6. Record the location of the surface that was cored, the surface type, and the core thickness in the field log book and on the core sampling record (Appendix C).

7. Place the core(s) into a clean labeled food-grade resealable 1-gallon bag (e.g., Ziploc®).

8. Place the Ziploc® bag with the sample into an empty 1-gallon Ziploc® bag. Place the two Ziploc® bags with the sample into a third 1-gallon Ziploc® bag so the sample is triple bagged and is ready for crushing (to be performed by the laboratory).

9. Place the sample into an ice bath immediately following sample collection until just before sample shipment.

10. Wear disposable powderless nitrile gloves while handling the sample and change gloves and bags between samples.

11. Inspect and document the condition of the sample material including photographic and written records.

12. Pack and ship samples in accordance with the procedures described in Section 16.5.

13. Complete chain-of-custody in accordance with procedures described in Section 16.6.

16.4.13.4 Quality Control Samples

Field quality control samples will include equipment blanks, field replicates (collocated samples), and matrix spike/matrix spike duplicate samples. Equipment or rinsate blanks will be collected by pouring deionized water, provided by the laboratory, over sampling equipment (i.e., coring bit) and collecting the equipment rinse water in appropriate containers with appropriate preservation.

Coded (double-blind) field replicates will be collocated in the field to evaluate core sample collection procedure precisions. Field replicate samples will be collected by taking a second 2-inch core directly adjacent to the original sample.

MS/MSD samples will be collected from sample locations that will yield enough core material for the laboratory to homogenize the entire sample core (i.e., building walls), and remove three aliquots (i.e., the sample, the MS, and the MSD) needed to perform the analysis. Samples to be analyzed as MS/MSDs will be collected following the same procedures outlined above and the sample will be labeled with the sample name and MS/MSD to indicate the sample as a quality control sample.

The quality control samples will be collected at a frequency consistent with Table 13 or the SS-WP.

16.4.13.5 Sample Analysis

Once the cores are received by the laboratory, the core samples will be prepared in accordance with the following procedure unless otherwise specified by the SS-WP. Core samples received by the laboratory will be in triplicate Ziploc® bags. Each triplicate Ziploc® bag with sample will be placed on a hardened concrete floor for crushing. A 4 lb hammer (or suitable equivalent) will be used to break up the core while making a reasonable effort to maintain the integrity of the bags. Rebar located within crushed cores, will be removed by hand when possible. The loose material is transferred to a clean #4 sieve (4.75 mm). Material passing the sieve will be collected in a certified clean wide mouth jar with a Teflon lined closure. The jar will be labeled with the corresponding sample identification and laboratory number. The material retained on the sieve is returned to the corresponding sample bag for further size reduction if more sample mass is required. In some instances the sample bags may require replacement. The process will continue until sufficient sample is obtained to provide for the requested analyses (a minimum of 30 grams for total polychlorinated biphenyls and polychlorinated terphenyls and a minimum of 100 grams for TCLP lead). Unused sample volume will be retained for reanalysis and sample archival.

The 4-pound hammer and #4 sieve will be decontaminated in the laboratory by dusting off both pieces of equipment and then rinsing them with reagent grade water. The equipment will then be scrubbed with an Alconox and water solution (or equivalent), followed by a second reagent grade water rinse. Lastly, the sampling equipment will be baked in an oven at 110ºC until dry.

16.5 SAMPLE HANDLING

16.5.1 Sample Volumes, Container Types, and Preservation Requirements

Types of sample containers, sample volumes, and methods of preservation are identified in Tables 5A and 5B. The laboratory will supply sample containers and preservatives in accordance with their own analytical procedures. A separate container may not be required for each parameter. The laboratory will add any necessary chemical preservatives prior to shipping the sample containers to the field.

16.5.2 Sample Packaging and Delivery

Samples will be delivered by common carrier to the designated laboratory for analysis daily or every other day, as required. The field team leader (or designee) will contact the laboratory to inform them of sample delivery before samples are to be picked up or delivered to the common carrier. The samples will be delivered in ice chests to the common carrier for overnight delivery. The chain-of-custody forms will be sealed in a plastic bag and taped to the inside lid of the chest. The chest will be sealed with custody seals and tamper-resistant tape, and the custody seals will be signed and dated by the sample custodian.

16.5.3 Sample Identification

Subsurface soil borings will be numbered consecutively beginning with SB-01 (soil borings) or MW-1 (monitoring well borings) or starting with the next consecutive number if existing borings/wells are present.

- Monitoring wells will be numbered consecutively beginning with MW-1.
- Test pits (TP) will be numbered consecutively beginning with TP-1
- Each sample will be given a unique alphanumeric identifier in accordance with the following classification system (such as ALBW-10001, see below):

SAMPLE IDENTIFICATION

LL* or NN*	LL	NNNNN	LL
Site Location	Activity Description /Sample Type	Sample Number	QC Identifier

Site Location:
AL – Ash Landfill
25 – SEAD-25
26 – SEAD-26

Activity Description/Sample Type:
BW - Biowall
MW - Monitoring Well Boring
MW - Monitoring Well
SB - Soil Boring
SW – Surface Water
TP - Test Pit
SD – Sediment
SS - Surface Soil

Sample Number: Sample type is designated based on a 5-digit numbering system. Sample numbers start with the next consecutive number.
0000# - Trip Blanks
0010# - Field or Rinseate Blanks
1000# - Soil Samples
2000# - Groundwater Samples
3000# - Surface Water Samples
4000# - Sediment/Ditchsoil Samples
5000# - Miscellaneous Samples (such as mulch or debris material).

QC Identifier: MS - Matrix Spike

MSD - Matrix Spike Duplicate

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* L = Letter
* N = Number

Additional sample identification information or coding maybe found in a SS-WP for a particular site. Field duplicate samples will be assigned identifiers that do not allow the laboratory to distinguish them as field duplicates. Each sample container will be labeled prior to packing for shipment. The sample identifier, site name, date and time of sampling, and analytical parameters will be written on the label in waterproof ink and recorded in the field book.

16.6 SAMPLE CUSTODY

Separate sample custody and documentation procedures will be followed for samples collected for field and laboratory analyses. Components of sample custody are sample labels and chain-of-custody forms.

For laboratory analysis, chain-of-custody forms will be completed for each shipment of samples to track the movement of samples and to provide a written record of all persons handling the samples. The chain-of-custody form will include sample information (sample identification, type, date, and time of collection), analyses requested, and the signature of each person receiving and relinquishing the samples.

The "Remarks" column of the chain-of-custody form will be used to record additional information that may be of use to the laboratory for prescreening the samples. When transferring samples, the individuals relinquishing and receiving the samples will sign, date, and note the time on the chain-of-custody form.

The original chain-of-custody form will accompany the samples to the laboratory. The laboratory will make and maintain a file copy, and the completed original will be returned to the task manager as a part of the final analytical report. This record serves to document sample custody transfer from the sampler to the shipper, and to the laboratory. Upon receipt of samples, the laboratory will provide a written report to the field investigation manager (or designee) summarizing the condition of samples, sample numbers received and corresponding laboratory numbers, and the estimated date for completion of laboratory analysis.

Sample custody within the laboratory may require an internal chain-of-custody. The sample custody documentation shall include the following:

- Name of associate taking custody of the sample from the sample storage area for preparation or analysis;
- Dates sample removed from and returned to the sample storage area;
- Identification of the tests to be performed on the sample aliquot(s) selected by the associate;
- Sample matrix;
- Laboratory sample numbers; and
- Sample storage location.

Access to the laboratory is restricted to prevent any unauthorized contact with samples, extracts, or documentation.

After the requested analyses on the samples have been completed, any remaining portions of the samples shall be stored for the amount of time required by the project and then disposed of by the laboratory. The disposal of each sample shall be recorded in the laboratory's project file or data management system. Disposal of samples shall occur in accordance with the laboratory procedures after the required retention period.

16.7 FIELD QUALITY CONTROL SAMPLES

16.7.1 Equipment Blank/Rinsate Blank

An equipment blank, or a rinsate blank, is a sample of ASTM Type II reagent grade water poured into or over or pumped through the sampling device, collected in a sample container, and transported to the laboratory for analysis. Equipment blanks are used to assess the effectiveness of equipment decontamination procedures. The frequency of collection for equipment blanks will be specified in the SS-WP. Equipment blanks shall be collected immediately after the equipment has been decontaminated. The blank shall be analyzed for all laboratory analyses requested for the environmental samples collected at the site.

16.7.2 Trip Blank

The trip blank consists of a VOC sample vial filled in the laboratory with ASTM Type II reagent grade water, transported to the sampling site, handled like an environmental sample and returned to the laboratory for analysis. Trip blanks are not opened in the field. Trip blanks are prepared only when VOC samples are taken and are analyzed only for VOC analytes. Trip blanks are used to assess the potential introduction of contaminants from sample containers or during the transportation and storage procedures. One trip blank shall accompany each cooler of samples sent to the laboratory for analysis of VOCs. In accordance with the USEPA Region 2 (1989) CERCLA Quality Assurance Manual, an aqueous trip blank is not required when non-aqueous samples are collected.

16.7.3 Field Duplicates

A field duplicate sample is a second sample collected at the same location as the original sample. Duplicate samples are collected simultaneously or in immediate succession, using identical recovery techniques, and treated in an identical manner during storage, transportation, and analysis. The sample containers are assigned an identification number in the field such that they cannot be identified (blind duplicate) as duplicate samples by laboratory personnel performing the analysis. Specific locations are designated for collection of field duplicate samples prior to the beginning of sample collection.

Duplicate sample results are used to assess precision of the sample collection process. Precision of soil samples to be analyzed for VOCs is assessed from collocated samples because the compositing process required to obtain uniform samples could result in loss of the compounds of interest. It is recommended to collect one sample per week or 10% of all field samples per matrix, whichever is greater (USEPA, 2004b).

16.7.4 Field Replicates

A field replicate sample, also called a split, is a single sample divided into two equal parts for analysis. The sample containers are assigned an identification number in the field such that they cannot be identified as replicate samples by laboratory personnel performing the analysis. Specific locations are designated for collection of field replicate samples prior to the beginning of sample collection. Replicate sample results are used to assess precision. The frequency of collection for field replicates is specified in Table 7-A through 7-G.

16.7.5 Matrix Spike and Matrix Spike Duplicate

Matrix spike and matrix spike duplicate samples will be collected from areas that are known or suspected to be contaminated. Additional volume will be required for aqueous samples and soil VOA samples designed for MS/MSD analyses. The extra volume containers will be marked as the sample number and the “MS/MSD”.

16.8 FIELD MEASUREMENTS

16.8.1 Parameters

The following is a list of all parameters that may be measured during field activities, as well as the equipment that will be used for the measurements:

Parameter	Equipment
Volatiles	MiniRae 2000 (or equivalent)
Water turbidity	Lamotte 2020 Turbidity Meter (or similar)
Water dissolved oxygen	Horiba U22 (or equivalent)
Temperature	Horiba U22 (or equivalent)
Specific Conductivity	Horiba U22 (or equivalent)
Oxygen Reduction Potential (ORP)	Horiba U22 (or equivalent)
pH	Horiba U22 (or equivalent)
Sulfate/sulfide	Hach® DR/850 Portable Colorimeter (or similar)
Nitrite	Hach® DR/850 Portable Colorimeter (or similar)
Alkalinity	Hach® DR/850 Portable Colorimeter (or similar)
Dissolved CO_2	Hach® Digital Titrator (or similar)
Nitrogen, Ammonia	Hach® Spectrophotometer (or similar)
Manganese	Hach® DR/4000 1-Inch Cell Adapter (or similar)
Ferrous iron	Hach® AccuVac Ampuls (or similar)
Air particulates	Personal Aerosol Monitor

The instruction manuals for the Lamotte 202 Turbidity Meter, the MiniRae 2000, the Horiba U-22, and the Hach® instruments are presented in Appendix G. Any additional equipment needed for a specific project or task shall be identified in the SS-WP.

16.8.2 Equipment Calibration and Quality Control

As required, field analytical equipment shall be calibrated according to the manufacturers' specifications prior to field use. This applies to equipment used for onsite measurements of DO, pH, specific conductance, ORP, and other field parameters. Initial and daily calibrations will be recorded in the field notebook. In addition the reference electrode utilized for ORP and the appropriate conversion factor will be recorded in the field notebook.

16.8.3 Field Monitoring Measurements

16.8.3.1 Groundwater Level Measurements

Water-level measurements shall be taken in all wells and piezometers to determine the elevation of the water table or piezometric surface at least once within a single 24-hour period. These measurements shall be taken after all wells and piezometers have been installed and developed and their water levels have recovered completely. Any conditions (e.g., barometric pressure) that may affect water levels

shall be recorded in the field log. The field log shall also include the previous water level measurement for each well (to determine if current water level is reasonable).

Water-level measurements shall be taken with electric sounders, air lines, pressure transducers, or water-level recorders (e.g., Stevens recorder). Devices that may alter sample composition shall not be used. Pressure gauges, manometers, or equivalent devices shall be used for flowing wells to measure the elevation of the piezometric surface. All measuring equipment shall be decontaminated according to the specifications in Section 16.3.11. Ground-water level shall be measured to the nearest 0.01 foot. (Two or more sequential measurements shall be taken at each location until two measurements agree to within + or - 0.01 foot.)

Static water levels shall be measured each time a well is sampled, and before any equipment enters the well. If the casing cap is airtight, allow time prior to measurement for equilibration of pressures after the cap is removed. Repeat measurements until water level is stabilized.

16.8.3.2 Floating Hydrocarbon Measurements

The thickness of hydrocarbons floating in monitor wells shall be measured with an electronic interface probe. Hydrocarbon detection paste, or any other method that may affect water chemistry, shall not be used. When detected, the presence of floating hydrocarbons shall be confirmed by withdrawing a sample with a clear, bottom-fill Teflon® bailer.

16.8.3.3 Groundwater Discharge Measurements

Groundwater discharge measurements shall be obtained during monitor well purging and aquifer testing. Groundwater discharges may be measured with orifice meters, containers of known volume, in-line meters, flumes, or Weirs, following the guidelines specified in the Water Measurement Manual (USDoI, 2001). Measurement devices shall be calibrated using containers of known volume.

16.8.3.4 Sulfate/Sulfide Measurements

Sulfide concentrations in groundwater cannot be measured using a probe and will be analyzed in the field via colorimetric analysis with a Hach® DR/850 Portable Colorimeter (or similar) after appropriate sample preparation. USEPA-approved Hach® Method 8131 (0 to 0.70 mg/L) will be used to analyze for sulfide. The manual for the colorimeter, including calibration procedures, and the procedures for Method 8131 are contained in Appendix G.

16.8.3.5 Nitrite Measurements

Nitrite concentrations in groundwater cannot be measured using a probe, so a Hach® DR/850 Portable Colorimeter (or similar) and Hach® Method 8507 (0 to 0.350 mg/L) will be utilized in the field to determine these concentrations. The manual for the colorimeter, including calibration procedures, and the procedures for Method 8507 are contained in Appendix G.

16.8.3.6 Alkalinity Measurements

Alkalinity of the groundwater sample will be measured in the field by via titrimetric analysis using USEPA-approved Hach® Method 8221 (0 to 5,000 mg/L as calcium carbonate), or equivalent. The procedures for this method are contained in Appendix G.

16.8.3.7 Portable Photoionization Analyzer

The photoionization analyzer will be a RaeSystems MiniRae 2000 (or equivalent), equipped with a 10.6 eV lamp. The MiniRae is capable of ionizing and detecting compounds with an ionization potential of less than 10.6 eV. This accounts for up to 73% of the volatile organic compounds on the Target Compound List.

Calibration must be performed at the beginning and end of each day of use with a standard calibration gas having an approximate concentration of 100 parts per million of isobutylene. If the unit experiences abnormal perturbation or erratic readings, additional calibration will be required.

All calibration data must be recorded in field notebooks and on calibration log sheets to be maintained on-site.

A battery check must be completed at the beginning and end of each working day.

16.8.3.8 Personal Aerosol Monitor

The operator shall ensure that the instruments respond properly to the substances that they are designed to monitor. Real time aerosol monitors must be zeroed at the beginning of each sampling period. The specific instructions for calibration and maintenance provided for each instrument should be followed.

All calibration data must be recorded in field notebooks and on calibration log sheets to be maintained on-site.

A battery check must be completed at the beginning and end of each working day.

16.8.3.9 pH Meter

Calibration of the pH meter must be performed at the start of each day of use, and after very high or low readings as required by this plan, according to manufacturer's instructions.

National Institute of Standards and Technology - traceable standard buffer solutions which bracket the expected pH range will be used. The standards will be pH of 4.0, 7.0 and 10.0 standard units.

The use of the pH calibration must be used to set the meter to display the value of the standard being checked. The calibration data must be recorded on calibration sheets maintained on-site or with the piece of equipment.

16.8.3.10 Specific Conductivity Meter and Temperature Probe

Calibration checks using the conductivity standard must be performed at the start of each day of use, after five to ten readings or after very high or low readings as required by this plan, according to manufacturer's instructions.

The portable conductivity meter must be calibrated using a reference solution of 200 uohms/cm on a daily basis. Readings must be within five percent to be acceptable. The thermometer of the meter must be calibrated against the field thermometer on a weekly basis.

16.8.3.11 Turbidity, Dissolved Oxygen, Dissolved CO_2, Ferrous Iron, Manganese, Sulfide, Ammonia, and Oxygen Reduction Potential Meters

These meters must be checked at the start of each day of use and at the end of the day.

16.8.4 Field Performance and System Audits

Field activities will be monitored on a per-task basis by the Technical Director or his/her designee to ensure compliance with this SAP and the SS-WP. Field performance and system audits will be conducted in accordance with the specifications presented in Section 9.1.2 and Section 9.2.2.

16.8.5 Field Environmental Data Reporting: Significant Digits Reflect Quantification Uncertainty

Field measurements of common water-quality parameters, other screening analytical data, calculations of aquifer properties (e.g., hydraulic conductivity, transmissivity, groundwater velocity), and quantities of contaminated soil and water removed and/or treated possess measurable uncertainty or error ranges. When reporting these data, therefore, the number of significant figures employed should reflect the true

accuracy and precision (reproducibility) of these measured and calculated values. As a general rule of thumb, field measurements of water quality parameters, quantities of contaminated media removed/remediated, screening analytical data and calculated aquifer properties rarely yield better than two-significant-figure accuracy and precision. Consequently, these field-measured parameters typically should be reported to two significant figures (e.g., DO, 2.1 mg/L; hydraulic conductivity, 120 ft/day; transmissivity, 1,100 ft^2/day; 130 tons of contaminated soil excavated) unless notably low uncertainty exists to justify reporting to three or more significant figures. Manufacturer's performance specifications that document high accuracy and precision for field meters may constitute an example of valid justification for reporting field values to three or more significant figures. Because pH and oxidation-reduction potential are logarithmic values, recommend reporting these parameters to three significant figures. In all cases, standard reporting practice should involve consistency in the number of significant figures used to report measured values.

Use of scientifically defensible and consistent numbers of significant figures in reporting analytical and quantitative field data allows the readers and users of these data to properly evaluate measurement uncertainty. This proper evaluation of data accuracy and precision facilitates the scientifically valid interpretation, summarization and subsequent reporting of these data. Field team members are encouraged to comply with *Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications* (ASTM Designation: E 29-02, 2002).

16.9 RECORD KEEPING

Bound field logbooks will be maintained by the field supervisor and other team members to provide a daily record of significant events, observations, and measurements during the field investigation. All entries will be signed and dated. All information pertinent to the field survey and/or sampling will be recorded in the logbooks. The logbooks will be bound, with sequentially numbered pages. Waterproof ink will be used in making all entries. Entries in the logbook will include, at a minimum, the items listed below:

<u>General information:</u>

- Names and titles of author and assistants;
- Date and time of entry;
- Physical/environmental conditions during field activity;
- Purpose of sampling activity;
- Location of sampling activity; and
- Names and titles of field crew.

Sampling documentation:

- Sample medium (e.g., groundwater, soil);
- Description of sampling point(s);
- Date and time of collection;
- Sample identification; and
- Sample analyses and containers.

Other information:

- Names and titles of site visitors;
- Field observations (i.e., unusual field conditions);
- Field measurements (such as pH, conductivity, temperature) and specific instrument calibration data;
- Field equipment (make, model, serial number);
- Equipment decontamination frequency; and
- Sample handling (e.g., preservation with ice) and shipping (i.e., shipping company, air bill number) information.

None of the field logbooks or forms will be destroyed or discarded, even if they are illegible or contain inaccuracies that require a replacement document. If a previously recorded entry is discovered to be incorrect, the incorrect entry will be crossed out in such a manner that it is still legible. The correct entry will be written in, and the change will be initialed and dated. If the change is made by someone other than the original author, or if the change is made on a subsequent day, a reason for the change will be recorded at the current active location in the logbook, with cross references.

Field personnel shall maintain field records sufficient to recreate all sampling and measurement activities. The requirements listed in this section apply to all measuring and sampling activities. Requirements specific to individual activities are listed in the section that addresses each activity. The information shall be recorded with indelible ink in a permanently bound notebook with sequentially numbered pages. These records shall be archived in an easily accessible form and made available to the Air Force upon request.

17.0 REQUIREMENTS FOR SITE-SPECIFIC WORK PLAN

This generic site-wide SAP will serve as an umbrella document under which project-specific tasks are conducted. This SAP will provide the majority of the QA/QC information and field sampling SOPs; the SS-WP should simply supplement this information by providing site-specific requirements. This section summarizes the key elements of SAP that should be covered in the SS-WP.

The following presents a list of the key elements of DQOs that should be included in the SS-WP, in accordance with the USEPA, NYSDEC, and USACE guidance documents.

1. Project/task description, which include a summary of all work to be performed, products to be produced, the schedule for implementation, the project's scope and project goals as well as how the project relates to the overall site investigation or remediation strategy;

2. Data use background, which should include sufficient background information to provide a historical, scientific, and regulatory perspective, project-specific data needs that have been identified (i.e., specific problem to be solved or outcome to be achieved), short-term decisions that will be made during the project planning phase, and long-term decisions that will be made prior to project closeout, a brief summary of the type of samples (media) and analyses (screening versus definitive, and applicable chemical parameters) that will be required to meet the data needs.

3. Project organization, including the designation of a project manager, quality assurance officer, and field analyst, (if field analysis is planned);

4. Site map showing sample locations;

5. An "Analytical Methods/Quality Assurance Summary Table" which should include the following information for all environmental, performance evaluation, and quality control samples:

    - matrix type;
    - number or frequency of samples to be collected per matrix;
    - number of field and trip blanks per matrix;
    - analytical parameters to be used per matrix;
    - analytical methods to be use per matrix;
    - the number and type of matrix spike and matrix spike duplicate samples to be collected;

- the number and type of duplicate samples to be collected;
- the number and type of split samples to be collected, if warranted;
- the number and type of performance evaluation samples to be analyzed, if warranted;
- sample preservation to be used per analytical method and sample matrix;
- sample container volume and type to be used per analytical method and sample matrix; and
- sample holding time to be used per analytical method and sample matrix.

6. A summary of QC activities needed for each sampling, analysis, or measurement technique.

7. Definition and requirement of data completeness for the project.

8. Information of the laboratory that will perform chemical analysis (laboratory name, address, contact information and current certifications for the analyses performed). A laboratory QA/QC manual should be included or cross-referenced to in accordance with the NYSDEC (2001) Development and Review of Site Analytical Plans.

9. Site-specific DQOs, which includes outputs from the systematic planning process used to design the study and measurement performance or acceptance criteria established as part of the study design. Information of this key element can be found in USEPA (2000a) QA/G-4, USEPA QA/G-5 Section 2.1.7, and USEPA (2005a) Uniform Federal Policy for Quality Assurance Project Plans Section 2.6.

10. Sampling process design (e.g., assumptions made, scale of representativeness, type of sampling design – probability-based or judgmental, sampling sites location method). Information of this key element can be found in USEPA (2002a) QA/G-5 Section 2.2.1 and USEPA (2005a) Uniform Federal Policy for Quality Assurance Project Plans Section 3.1.1.

11. Specialized training or certification, if needed and plans for providing, documenting, and assuring this training.

12. Existing data that will be obtained from non-measurement sources, intended use of non-direct measurements, and acceptance criteria and any limitations for using such data. Information of this key element can be found in USEPA (2002a) QA/G-5 Section 2.2.9.

13. Reconciliation with user requirements. Information of this key element can be found in USEPA (2002a) QA/G-5 Section 2.4.3.

14. Any QA/QC and field sampling protocols that are different from or not covered in this SAP (e.g., sampling procedures and methods, sample storage and handling, sample delivery, and equipment decontamination procedures).

15. Criteria for comparability between screening data and definitive data, when definitive analysis is performed to confirm screening results.

16. Requirement for laboratory reporting limits or method detection limits.

17. SS-WP distribution list and sign-off sheet.

18. Decontamination area designated for specific sampling events and any modification of decontamination methods.

19. Waste disposal companies and disposal facilities, if warranted.

20. Instruction, operational manual, and operational requirements for any equipments that will be used for the site and are not covered in this SAP.

21. QA/QC requirements for any screening and definitive analytical methods not covered in this SAP. And

22. Any variances from this SAP such as: 1) if field audits are warranted, SOPs for field audit will be specified in the SS-WP; 2) sediment sampling depth should be specified if samples are not to be collected with 6 inches; etc.

23. Specification of instrument makes and models, instrument manuals, and survey-specific procedures for radiological surveys.

18.0 REFERENCES

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Table 1-A. Potential Chemical-Specific Data Quality Objectives for Soil/Sediment

Analyte	Abbreviation	CAS #	Human Health Screening Values						Most Stringent Human Health Criteria	Potential ARAR/TBC for Soil *	Potential ARAR/TBC for Sediment **	Ecological Screening Values (Terrestrial)	Eco SV Source
			Residential Soil (mg/kg)			Industrial Soil (mg/kg)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	Region 9 PRG	Region 3 RBC	Region 6 SSL (3)	Soil - Direct Contact (mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	
VOCs													
Benzene		71-43-2	0.64	12	0.66	1.4	52	1.5	0.64	0.06	1.095	0.1	E
1,1-Dichloroethane	DCA	75-34-3	510	16000	590	1700	200000	2100	510	0.2	N/A	0.3	E
1,1-Dichloroethene	DCE	75-35-4	120	3900	280	410	51000	430	120	0.4	N/A	0.1	I
1,2-Dichloroethane	DCA	107-06-2	0.28	7	0.35	0.6	31	0.77	0.28	0.1	N/A	870	E
Cis-1,2-Dichloroethene	cis-DCE	156-59-2	43	780	43	150	10000	150	43	N/A	N/A	0.3	E
Trans-1,2-Dichloroethene	trans-DCE	156-60-5	69	1600	63	230	20000	210	63	0.3	N/A	0.3	E
Ethyl benzene	EB	100-41-4	400	7800	230	400	100000	230	230	5.5	0.939	0.1	E
1,1,1-Trichloroethane	TCA	71-55-6	1200	22000	1400	1200	290000	1400	1200	0.8	N/A	29.8	F
Trichloroethene	TCE	79-01-6	0.053	1.6	0.043	0.11	7.2	0.092	0.043	0.7	N/A	0.3	E
Toluene	TOL	108-88-3	520	16000	520	520	200000	520	520	1.5	1.916	0.1	E
Xylenes		1330-20-7	270	16000	210	420	200000	210	210	1.2	N/A	0.1	E
Vinyl chloride	VC	75-01-4	0.079	0.09	0.15	0.75	4	0.43	0.079	0.2	N/A	0.3	E
SVOCs													
Acenaphthene		83-32-9	3700	4700	3700	29000	61000	33000	3700	50	5.475	20	J
Acenaphthylene		208-96-8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	41	N/A	0.1	E
Anthracene		120-12-7	22000	23000	22000	100000	310000	100000	22000	50	4.184	0.1	E
Benzo(a)anthracene		56-55-3	0.62	0.87	0.62	2.1	3.9	2.3	0.62	0.224	0.469	0.1	E

Table 1-A. Potential Chemical-Specific Data Quality Objectives for Soil/Sediment

Analyte	Abbreviation	CAS #	Human Health Screening Values						Most Stringent Human Health Criteria	Potential ARAR/TBC for Soil *	Potential ARAR/TBC for Sediment **	Ecological Screening Values (Terrestrial)	Eco SV Source
			Residential Soil (mg/kg)			Industrial Soil (mg/kg)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	Region 9 PRG	Region 3 RBC	Region 6 SSL (3)	Soil - Direct Contact (mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	
Benzo(a)pyrene	BaP	50-32-8	0.062	0.087	0.062	0.21	0.39	0.23	0.062	0.061	N/A	0.1	E
Benzo(b)fluoranthene		205-99-2	0.62	0.87	0.62	2.1	3.9	2.3	0.62	1.1	N/A	0.1	E
Benzo(ghi)perylene		191-24-2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	50	N/A	0.1	E
Benzo(k)fluoranthene		207-08-9	6.2	8.7	6.2	21	39	23	6.2	1.1	N/A	0.1	E
Carbazole		86-74-8	24	32	24	86	140	96	24	N/A	N/A	N/A	N/A
Chrysene		218-01-9	62	87	62	210	390	230	62	0.4	N/A	0.1	E
Dibenz(a,h)anthracene		53-70-3	0.062	0.087	0.062	0.21	0.39	0.23	0.062	0.014	N/A	0.1	E
Fluoranthene		206-44-0	2300	3100	2300	22000	41000	24000	2300	50	39.887	0.1	E
Fluorene		86-73-7	2700	3100	2600	26000	41000	26000	2600	50	0.313	30	J
Indeno(1,2,3-cd)pyrene		193-39-5	0.62	0.87	0.62	2.1	3.9	2.3	0.62	3.2	N/A	0.1	E
Naphthalene		91-20-3	56	1600	120	190	20000	190	56	13	1.173	0.1	E
Phenanthrene		85-01-8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	50	4.693	0.1	E
Pyrene		129-00-0	2300	2300	2300	29000	31000	32000	2300	50	37.58	0.1	E
PCB													
Aroclor-1260		11096-82-5	0.22	0.32	0.22	0.74	1.4	0.83	0.22	1.0	0.055	0.1	E
Pesticides													
4,4'-DDD		72-54-8	2.4	2.7	2.4	10	12	11	2.4	2.9	0.039	0.1	E
4,4'-DDE		72-55-9	1.7	1.9	1.7	7	8.4	7.8	1.7	2.1	0.039	0.1	E

Table 1-A. Potential Chemical-Specific Data Quality Objectives for Soil/Sediment

Analyte	Abbreviation	CAS #	Human Health Screening Values						Most Stringent Human Health Criteria	Potential ARAR/TBC for Soil *	Potential ARAR/TBC for Sediment **	Ecological Screening Values (Terrestrial)	Eco SV Source
			Residential Soil (mg/kg)			Industrial Soil (mg/kg)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	Region 9 PRG	Region 3 RBC	Region 6 SSL (3)	Soil - Direct Contact (mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	
4,4'-DDT		50-29-3	1.7	1.9	1.7	7	8.4	7.8	1.7	2.1	0.039	0.1	E
Heptachlor epoxide		1024-57-3	0.053	0.07	0.053	0.19	0.31	0.21	0.053	0.02	0.0012	0.1	E
Explosives													
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4	4.4	5.8	4.4	16	26	17	4.4	N/A	N/A	5.8	A
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0	3100	3900	3100	31000	51000	34000	3100	N/A	N/A	43	H
2,4,6-Trinitrotoluene (4)	2,4,6-TNT	118-96-7	16	21	16	57	95	64	16	N/A	N/A	8	B
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4	1800	2300	1800	18000	31000	21000	1800	N/A	N/A	0.376	F
1,3-Dinitrobenzene	1,3-DNB	99-65-0	6.1	7.8	6.1	62	100	68	6.1	N/A	N/A	0.655	F
2,4-Dinitrotoluene (1)	2,4-DNT	121-14-2	0.72	0.94	0.72	2.5	4.2	2.8	0.72	N/A	N/A	1.28	F
2,6-Dinitrotoluene (1)	2,6-DNT	606-20-2	0.72	0.94	0.72	2.5	4.2	2.8	0.72	1.0	N/A	0.0328	F
2-Amino-4,6-dinitrotoluene	2-Am-DNT	35572-78-2	12	160	N/A	120	2000	N/A	12	N/A	N/A	5.3	H
2-Nitrotoluene	2-NT	88-72-2	0.88	2.8	2.8	2.2	12	14	0.88	N/A	N/A	4.1	H
3-Nitrotoluene	3-NT	99-08-1	730	1600	1600	1000	20000	23000	730	N/A	N/A	5.3	H
4-Amino-2,6-dinitrotoluene	4-Am-DNT	19406-51-0	12	160	N/A	120	2000	N/A	12	N/A	N/A	N/A	N/A
4-Nitrotoluene	4-NT	99-99-0	12	38	38	30	170	190	12	N/A	N/A	9.4	H
Nitrobenzene	NB	98-95-3	20	39	20	100	510	110	20	0.2	N/A	40	C

Table 1-A. Potential Chemical-Specific Data Quality Objectives for Soil/Sediment

Analyte	Abbreviation	CAS #	Human Health Screening Values						Most Stringent Human Health Criteria	Potential ARAR/TBC for Soil *	Potential ARAR/TBC for Sediment **	Ecological Screening Values (Terrestrial)	Eco SV Source
			Residential Soil (mg/kg)			Industrial Soil (mg/kg)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	Region 9 PRG	Region 3 RBC	Region 6 SSL (3)	Soil - Direct Contact (mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	
Nitroglycerin	NG	55-63-0	35	46	N/A	120	200	N/A	35	N/A	N/A	150	H
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8	610	310	240	6200	4100	2700	240	N/A	N/A	2	H
Pentaerythritol Tetranitrate	PETN	78-11-5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	21000	H
Inorganics													
Aluminum	Al	7429-90-5	76000	78000	76000	100000	1000000	100000	76000	SB	N/A	50	C
Antimony	Sb	7440-36-0	31	31	31	410	410	450	31	SB	2	0.27	A
Arsenic	As	7440-38-2	0.39	0.43	0.39	1.6	1.9	1.8	0.39	7.5 or SB	6	18	A
Barium	Ba	7440-39-3	5400	5500	5500	67000	72000	79000	5400	300	N/A	330	A
Beryllium	Be	7440-41-7	150	160	150	1900	2000	2200	150	0.16 or SB	N/A	1.1	C
Cadmium	Cd	7440-43-9	37	39	39	450	510	560	37	1 or SB	0.6	1.6	C
Calcium	Ca	7440-70-2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	SB	N/A	N/A	N/A
Chromium (2)	Cr	7440-47-3	210	230	210	450	3100	450	210	10 or SB	26	26	A
Cobalt	Co	7440-48-4	900	1600	900	1900	20000	1900	900	30	N/A	13	A
Copper	Cu	7440-50-8	3100	3100	2900	41000	41000	42000	2900	25 or SB	16	61	A
Iron	Fe	7439-89-6	23000	23000	23000	100000	310000	100000	23000	2000 or SB	20000	N/A	N/A
Lead	Pb	7439-92-1	400	N/A	400	800	N/A	800	400	SB	31	11	A
Magnesium	Mg	7439-95-4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	SB	N/A	4400	E

Table 1-A. Potential Chemical-Specific Data Quality Objectives for Soil/Sediment

Analyte	Abbreviation	CAS #	Human Health Screening Values						Most Stringent Human Health Criteria	Potential ARAR/TBC for Soil *	Potential ARAR/TBC for Sediment **	Ecological Screening Values (Terrestrial)	Eco SV Source
			Residential Soil (mg/kg)			Industrial Soil (mg/kg)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	Region 9 PRG	Region 3 RBC	Region 6 SSL (3)	Soil - Direct Contact (mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	
Manganese	Mn	7439-96-5	1800	1600	3200	19000	20000	35000	1600	SB	460	152	A
Molybdenum	Mo	7439-98-7	390	390	390	5100	5100	5700	390	N/A	N/A	0.59	E
Nickel	Ni	7440-02-0	1600	1600	1600	20000	20000	23000	1600	13 or SB	16	38	A
Potassium	K	7440-09-7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	SB	N/A	N/A	N/A
Selenium	Se	7782-49-2	390	390	390	5100	5100	5700	390	2	N/A	0.50	A
Silver	Ag	7440-22-4	390	390	390	5100	5100	5700	390	SB	1	2.0	C
Sodium	Na	7440-23-5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	SB	N/A	N/A	N/A
Strontium	Sr	7440-24-6	47000	47000	47000	100000	610000	100000	47000	N/A	N/A	N/A	N/A
Thallium	Tl	7440-28-0	5.2	5.5	N/A	67	72	N/A	5.2	SB	N/A	1.0	C
Titanium	Ti	7440-32-6	100000	310000	N/A	100000	4100000	N/A	100000	N/A	N/A	N/A	N/A
Vanadium	V	7440-62-2	78	78	78	1000	1000	1100	78	150	N/A	2.0	C
Zinc	Zn	7440-66-6	23000	23000	23000	100000	310000	100000	23000	SB	120	120	A
Zirconium	Zr	7440-67-7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Mercury	Hg	7439-97-6	23	23	23	310	310	340	23	0.1	0.15	0.10	C
Phosphorus (White)	WP or P4	7723-14-0	1.6	1.6	1.6	20	20	23	1.6	N/A	N/A	N/A	N/A
Perchlorate	ClO4	14797-73-0	7.8 (5)	55	7.8	100	720	110	7.8	N/A	N/A	N/A	N/A

* Potential ARAR/TBC values are from NYSDEC Technical and Administrative Guidance Memorandum (TAGM) #4046

(on-line resources available at http://www.dec.state.ny.us/website/der/tagms/prtg4046.html)
** Potential ARAR/TBC values for NYSDEC Technical Guidance for Screening Contaminated Sediment. All values except for inorganic values were calculated based on a Total Organic Carbon of 39,105 mg/Kg (SEDA site average).

(1) Carcinogenic DNT mixture values used if more conservative than noncarcinogenic isomer-specific values
(2) Total chromium values used if available. All Region 3 values are based on hexavalent chromium.
(3) Lower of the industrial values provided (industrial w/o dermal vs. industrial/outdoor)
(4) Noncancer RBCs at an HI of 0.1 provided because screening at an HI of 0.1, in accordance with Region 3 guidance, will result in noncancer RBCs being lower than the cancer RBCs
(5) Perchlorate Region 9 PRG value is based on perchlorate acid.

Region 9 PRGs, dated January, 2005
Region 3 RBCs, dated April 2005
Region 6 SSLs, dated 21 December 2004

Eco Screening Value Sources:

A USEPA EcoSSLs
B Los Alamos Nuclear Lab Screening Level
C USEPA Region 4 Eco Screening Values
D San Francisco Regional Water Quality Control Board Surface Water Screening Values
E USEPA Region 3 Freshwater Screening Benchmarks
F USEPA Region 5 Ecological Data Quality Levels
G Talmage, et. al. 1999
H Los Alamos National Laboratory (LANL), ECORISK Database, 2004
I. CCME, 2003
J. Oak Ridge, 1997

Table 1-B. Potential Chemical-Specific Data Quality Objectives for Groundwater/Surface Water

Analyte	Abbreviation	CAS #	Human Health Screening Values					Federal Ambient Water Quality (ug/L)		NYSDEC GA Standards (ug/L)*	NYSDEC Class C Surface Water Standard (ug/L)	Ecological Screening Values (ug/L)	Eco SV Source
			Tap Water (ug/L)			Federal Drinking Water Criteria (ug/L)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	MCLs	HA	CMC	CCC				
VOCs													
Benzene		71-43-2	0.35	0.34	0.35	5	100(6)	N/A	N/A	1	210**	370	E
1,1-Dichloroethane	DCA	75-34-3	810	900	810	N/A	N/A	N/A	N/A	5	N/A	47	E
1,1-Dichloroethene	DCE	75-35-4	340	350	340	7	6(6)	N/A	N/A	5	N/A	25	E
1,2-Dichloroethane	DCA	107-06-2	0.12	0.12	0.12	5	40(6)	N/A	N/A	0.6	N/A	100	E
Cis-1,2-Dichloroethene	cis-DCE	156-59-2	61	61	61	70	70	N/A	N/A	5	N/A	590	E
Trans-1,2-Dichloroethene	trans-DCE	156-60-5	120	110	120	100	100	N/A	N/A	5	N/A	970	E
Ethyl benzene	EB	100-41-4	1300	1300	1300	700	700	N/A	N/A	5	17**	90	E
1,1,1-Trichloroethane	TCA	71-55-6	3200	3200	840	200	200	N/A	N/A	5	N/A	11	F
Trichloroethene	TCE	79-01-6	0.028	0.026	0.028	5	300(6)	N/A	N/A	5	N/A	21	E
Toluene	TOL	108-88-3	720	750	720	1000	1000	N/A	N/A	5	100**	2	E
Xylenes		1330-20-7	210	210	200	10000	7000(7)	N/A	N/A	5	65**(11)	13	E
Vinyl chloride	VC	75-01-4	0.02	0.015	0.043	2	2(6)	N/A	N/A	2	N/A	930	E
SVOCs													
Acenaphthene		83-32-9	370	370	370	N/A	2000(7)	N/A	N/A	20**	5.3**	5.8	E
Acenaphthylene		208-96-8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	4840	F
Anthracene		120-12-7	1800	1800	1800	N/A	10000(7)	N/A	N/A	50**	3.8**	0.012	E
Benzo(a)anthracene		56-55-3	0.092	0.092	0.092	N/A	N/A	N/A	N/A	0.002**	0.03**	0.018	E
Benzo(a)pyrene	BaP	50-32-8	0.0092	0.0092	0.0092	0.2	0.5(6)	N/A	N/A	ND	N/A	0.014	F
Benzo(b)fluoranthene		205-99-2	0.092	0.092	0.092	N/A	N/A	N/A	N/A	0.002**	N/A	9.07	F

Table 1-B. Potential Chemical-Specific Data Quality Objectives for Groundwater/Surface Water

Analyte	Abbreviation	CAS #	Human Health Screening Values					Federal Ambient Water Quality (ug/L)		NYSDEC GA Standards (ug/L)*	NYSDEC Class C Surface Water Standard (ug/L)	Ecological Screening Values (ug/L)	Eco SV Source
			Tap Water (ug/L)			Federal Drinking Water Criteria (ug/L)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	MCLs	HA	CMC	CCC				
Benzo(ghi)perylene		191-24-2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	7.64	F
Benzo(k)fluoranthene		207-08-9	0.92	0.92	0.92	N/A	N/A	N/A	N/A	0.002**	N/A	0.05	H
Carbazole		86-74-8	3.4	3.3	3.4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Chrysene		218-01-9	9.2	9.2	9.2	N/A	N/A	N/A	N/A	0.002 **	N/A	N/A	N/A
Dibenz(a,h)anthracene		53-70-3	0.0092	0.0092	0.0092	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Fluoranthene		206-44-0	1500	1500	1500	N/A	N/A	N/A	N/A	50**	N/A	0.04	E
Fluorene		86-73-7	240	240	240	N/A	1000(7)	N/A	N/A	50**	0.54**	3	E
Indeno(1,2,3-cd)pyrene		193-39-5	0.092	0.092	0.092	N/A	N/A	N/A	N/A	0.002**	N/A	4.31	F
Naphthalene		91-20-3	6.2	6.5	6.2	N/A	100	N/A	N/A	10**	13**	1.1	E
Phenanthrene		85-01-8	N/A	N/A	N/A	N/A	N/A	N/A	N/A	50**	5**	0.4	E
Pyrene		129-00-0	180	180	180	N/A	N/A	N/A	N/A	50**	4.6**	0.025	E
PCB													
Aroclor-1260		11096-82-5	0.034	0.033	0.034	0.5	10(6)	N/A	0.014	5	1.2E-4	7.4E-5	E
Pesticides													
4,4'-DDD		72-54-8	0.28	0.28	0.28	N/A	N/A	N/A	N/A	0.3	1.1E-5(12)	0.011	E
4,4'-DDE		72-55-9	0.2	0.2	0.2	N/A	N/A	N/A	N/A	0.2	1.1E-5(12)	1050	E
4,4'-DDT		50-29-3	0.2	0.2	0.2	N/A	N/A	1.1	0.001	0.2	1.1E-5(12)	0.001	E
Heptachlor epoxide		1024-57-3	0.0074	0.0074	0.0074	0.2	0.4(6,7)	0.52	0.0038	0.03	N/A	0.0038	E
Explosives													
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4	0.61	0.61	0.61	N/A	2	N/A	N/A	5	N/A	360	E
Octahydro-1,3,5,7-tetranitro-1,3,5,7-	HMX	2691-41-0	1800	1800	1800	N/A	400	N/A	N/A	N/A	N/A	150	E

Table 1-B. Potential Chemical-Specific Data Quality Objectives for Groundwater/Surface Water

Analyte	Abbreviation	CAS #	Human Health Screening Values					Federal Ambient Water Quality (ug/L)		NYSDEC GA Standards (ug/L)*	NYSDEC Class C Surface Water Standard (ug/L)	Ecological Screening Values (ug/L)	Eco SV Source
			Tap Water (ug/L)			Federal Drinking Water Criteria (ug/L)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	MCLs	HA	CMC	CCC				
tetrazocine													
2,4,6-Trinitrotoluene (4)	2,4,6-TNT	118-96-7	2.2	2.2	2.2	N/A	2	N/A	N/A	5	N/A	100	E
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4	1100	1100	1100	N/A	N/A	N/A	N/A	5	N/A	11	G
1,3-Dinitrobenzene	1,3-DNB	99-65-0	3.6	3.7	3.7	N/A	1	N/A	N/A	5	N/A	20	G
2,4-Dinitrotoluene (1)	2,4-DNT	121-14-2	0.099	0.098	0.099	N/A	5 (6)	N/A	N/A	5	N/A	310	C
2,6-Dinitrotoluene (1)	2,6-DNT	606-20-2	0.099	0.098	0.099	N/A	5 (6)	N/A	N/A	5	N/A	81	E
2-Amino-4,6-dinitrotoluene	2-Am-DNT	35572-78-2	7.3	7.3	N/A	N/A	N/A	N/A	N/A	5	N/A	20	G
2-Nitrotoluene	2-NT	88-72-2	0.049	0.046	0.29	N/A	N/A	N/A	N/A	5	N/A	N/A	
3-Nitrotoluene	3-NT	99-08-1	120	120	120	N/A	N/A	N/A	N/A	5	N/A	750	E
4-Amino-2,6-dinitrotoluene	4-Am-DNT	19406-51-0	7.3	7.3	N/A	N/A	N/A	N/A	N/A	5	N/A	N/A	
4-Nitrotoluene	4-NT	99-99-0	0.66	0.62	4.0	N/A	N/A	N/A	N/A	5	N/A	1900	E
Nitrobenzene	NB	98-95-3	3.4	3.5	3.4	N/A	N/A	N/A	N/A	0.4	N/A	270	C
Nitroglycerin	NG	55-63-0	4.8	4.8	N/A	N/A	5	N/A	N/A	N/A	N/A	138	E
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8	360	150	150	N/A	N/A	N/A	N/A	5	N/A	5800	H
Pentaerythritol Tetranitrate	PETN	78-11-5	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	85000	E
Inorganics													
Aluminum	Al	7429-90-5	36000	37000	37000	50 (5)	N/A	750(9)	87(9)	N/A	100	87	E
Antimony	Sb	7440-36-0	15	15	15	6	6	N/A	N/A	3	N/A	6.0	D
Arsenic	As	7440-38-2	0.045	0.045	0.045	10	10(7)	340	150	25	150	0.14	D

Table 1-B. Potential Chemical-Specific Data Quality Objectives for Groundwater/Surface Water

Analyte	Abbreviation	CAS #	Human Health Screening Values					Federal Ambient Water Quality (ug/L)		NYSDEC GA Standards (ug/L)*	NYSDEC Class C Surface Water Standard (ug/L)	Ecological Screening Values (ug/L)	Eco SV Source
			Tap Water (ug/L)			Federal Drinking Water Criteria (ug/L)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	MCLs	HA	CMC	CCC				
Barium	Ba	7440-39-3	2600	2600	2600	2000	2000	N/A	N/A	1000	N/A	1000	D
Beryllium	Be	7440-41-7	73	73	73	4	70(7)	N/A	N/A	3	1100(13)	2.7	D
Cadmium	Cd	7440-43-9	18	18	18	5	5	2.0	0.25	5	3.85(13)	2.2	D
Calcium	Ca	7440-70-2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Chromium (2)	Cr	7440-47-3	110	110	110	100	100(7)	16	11	50	140(13)	50	D
Cobalt	Co	7440-48-4	730	730	730	N/A	N/A	N/A	N/A	N/A	5	3.0	D
Copper	Cu	7440-50-8	1500	1500	1400	1300 1000 (5)	N/A	13	9.0	200	17.36(13)	9.0	D
Iron	Fe	7439-89-6	11000	11000	11000	300 (5)	N/A	N/A	1000(9)	300	300	300	E
Lead	Pb	7439-92-1	N/A	N/A	15	15	N/A	65	2.5	25	8.7(13)	2.5	D
Magnesium	Mg	7439-95-4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	35000**	N/A	N/A	N/A
Manganese	Mn	7439-96-5	880	730	1700	50 (5)	300	N/A	N/A	300	N/A	120	E
Mercury	Hg	7439-97-6	11	11	11	2	2	1.4	0.77	0.7	0.0026	0.77	D
Molybdenum	Mo	7439-98-7	180	180	180	N/A	40	N/A	N/A	N/A	N/A	N/A	N/A
Nickel	Ni	7440-02-0	730	730	730	N/A	100	470	52	100	100.16(13)	52	D
Potassium	K	7440-09-7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Selenium	Se	7782-49-2	180	180	180	50	50	N/A	5.0	10	4.6	5.0	D
Silver	Ag	7440-22-4	180	180	180	100 (5)	100	3.2	N/A	50	0.1	0.34	D
Sodium	Na	7440-23-5	N/A	N/A	N/A	20000 (8)	N/A	N/A	N/A	20000	N/A	N/A	N/A
Strontium	Sr	7440-24-6	22000	22000	22000	N/A	4000	N/A	N/A	N/A	N/A	N/A	N/A
Thallium	Tl	7440-28-0	2.4	2.6	2.9	2	0.5	N/A	N/A	0.5**	8	2.0	D
Titanium	Ti	7440-32-6	150000	150000	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Vanadium	V	7440-62-2	36	37	37	N/A	N/A	N/A	N/A	N/A	14	19	D

Table 1-B. Potential Chemical-Specific Data Quality Objectives for Groundwater/Surface Water

Analyte	Abbreviation	CAS #	Human Health Screening Values					Federal Ambient Water Quality (ug/L)		NYSDEC GA Standards (ug/L)*	NYSDEC Class C Surface Water Standard (ug/L)	Ecological Screening Values (ug/L)	Eco SV Source
			Tap Water (ug/L)			Federal Drinking Water Criteria (ug/L)							
			Region 9 PRG	Region 3 RBC	Region 6 SSL	MCLs	HA	CMC	CCC				
Zinc	Zn	7440-66-6	11000	11000	11000	5000 (5)	2000	120	120	2000**	159.6(13)	120	D
Zirconium	Zr	7440-67-7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Phosphorus (White)	WP or P4	7723-14-0	0.73	0.73	0.73	N/A	0.1	N/A	N/A	N/A	N/A	N/A	N/A
Perchlorate	ClO4	14797-73-0	3.6 (10)	26	3.7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

* New York State Ambient Water Quality Standards, GA (http://www.dec.state.ny.us/website/regs/part701.html)
** Guidance value in NYSDEC AWQS, Class GA groundwater or Class C surface water.

(1) Carcinogenic DNT mixture values used if more conservative than noncarcinogenic isomer-specific values
(2) Total chromium values used if available. All Region 3 values are based on hexavalent chromium.
(3) Lower of the industrial values provided (industrial w/o dermal vs. industrial/outdoor)
(4) Noncancer RBCs at an HI of 0.1 provided because screening at an HI of 0.1, in accordance with Region 3 guidance, will result in noncancer RBCs being lower than the cancer RBCs
(5) All MCLs are primary except those with this footnote.
(6) All HAs are lifetime except those footnoted, which are based on 10-4 cancer risk
(7) Drinking Water Equivalent Level
(8) Drinking Water Advisory
(9) Non-Priority pollutant
(10) Perchlorate Region 9 PRG value is based on perchlorate acid.
(11) Xlyene Class C surface water value used 1,4-Xlyene (106-42-3).
(12) 4,4-DDD, -DDE, -DDT Class C surface water values based on the sum of DDD, DDE, and DDT equal to 1.1E-5 ug/L.
(13) Inorganic Class C surface water values are based on an assumed hardness of 217 mg/L.

Sources:
A USEPA EcoSSLs
B Los Alamos Nuclear Lab Screening Level
C USEPA Region 4 Eco Screening Values
D San Francisco Regional Water Quality Control Board Surface Water Screening Values
E USEPA Region 3 Freshwater Screening Benchmarks, 2005
F USEPA Region 5 Ecological Data Quality Levels
G Talmage, et. al. 1999
H. Dutch, 2000.

ND – Not detected by approved analytical methods SB – Site Background N/A – Not Applicable

Region 9 PRGs, dated January 2005 Region 6 SSLs, dated 21 December 2004 Region 3 RBCs, dated April 2005

Table 2
Project Communication Pathways

Communication Drivers	Responsible party	Name	Phone Number	Procedure
Approval of QAPP/amendments to QAPP	USEPA PM NYSDEC PM SEDA PM	Julio F. Vazquez Kuldeep K. Gupta Steve Absolom	212-637-4323 518-402-9620 607-869-1309	Parsons PM will initiate calls to SEDA if review time passed the scheduled review period. SEDA will then call USEPA and NYSDCE PM to discuss QAPP/amendment schedule.
Notification of delays or changes to field work	Parsons PM	Todd Heino	617-449-1405	Parsons field team leader will update PM daily filed progress. Parsons PM will update SEDA any delay or change of field activities.
Recommendations to stop work and initiation of corrective action	Parsons PM Parsons Health and Safety Officer	Todd Heino	617-449-1405	Parsons PM or Health and Safety Officer will initiate a work stoppage due to QA/QC concerns, health and safety concerns, or any other project related concerns.
Reporting of issues related to analytical data quality	Parsons Chemist	Chunhua Liu	617-449-1567	Parsons chemist will initiate discussion with the Laboratory with any data quality issues.
Quality Assurance and Changes to the QAPP	PARSONS Quality Assurance Officer	John Lanier	716-633-7074 X 222	Parsons QA Officer will not be involved in the data generation process. However, the QA Officer will initiate internal discussion with PM and project team regarding any QA issues and corrective actions.

Table 3
Summary of Screening Analytical Methods and Method Quantitation Limits

Reference Number	Title, Revision Date, and/or Number	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project? (Y/N)	Method Quantitation Limits [1]
USEPA Method 160.1/160.3/ASTM D2216-90/D2216-05	Residue, Total (Gravimetric, Dried at 103-105°C), Approved for NPDES (Issued 1971) Standard method for laboratory determination of water (moisture) content of soil and rock	Percent Solids	Drying Oven	Laboratory	No	0.1%
SW846 Method 1010A/ 1020B/ 1030	Pensky-Martens Closed-Cup Method For Determining Ignitability, Revision 1, 2002; Small Scale Closed-Cup Method For Determining Ignitability, Revision 2, 2002; Ignitability of Solids, Revision 0, 1996	Ignitability	Pensky-Martens Closed-Cup Tester; Small Scale Closed-Cup Apparatus; A Bunsen burner	Laboratory	No	1ºF
SW846 Method 1110	Corrosivity Toward Steel, Revision 0, 1996	Corrosivity	A resin flask	Laboratory	No	
SW846 Method 9040C	Electrometric Measurement, Revision 3, 2002	pH (water)	pH meter	Laboratory/Field	No	
SW846 Method 9045D	Soil and Waste pH, Revision 4, 2002	pH (soil)	pH meter	Laboratory/Field	No	
SW846 Method 9050A	Specific Conductance, Revision 1, 1996	conductance	Self-contained conductivity instruments	Laboratory/Field	No	
USEPA Method 130.1	Hardness, Total (mg/L as $CaCO_3$) (Colorimetric, Automated EDTA) - Approved for NPDES (Issued 1971)	Hardness	Spectrophotometer	Laboratory/Field	No	10 mg/L
USEPA Method 170.1	Temperature - Approved for NPDES (Issued 1974)	Temperature	Thermometer	Laboratory/Field	No	
USEPA Method 180.1	Determination Of Turbidity By Nephelometry, Revision 2, 1993.	Turbidity	Nephelometry	Laboratory/Field	No	
E310.1/Hach Method 8203/8221 or similar	Alkalinity (Titrimetric, pH 4.5) - Approved for NPDES (Editorial Revision 1978)	Alkalinity	PH meter or electrically operated titrator	Laboratory/Field	No	10 mg/L

Table 3
Summary of Screening Analytical Methods and Method Quantitation Limits

Reference Number	Title, Revision Date, and/or Number	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project? (Y/N)	Method Quantitation Limits [1]
E360.1 with commercially available probe	Oxygen, Dissolved (Membrane Electrode) - Approved for NPDES (Issued 1971)	Dissolved oxygen	Oxygen Analyzer	Laboratory/Field	No	
Organic Vapor Analysis	SOP (Section 16 of this SAP)	Hydrocarbon vapor	Photoionization Detector (PID)	Field	No	0.05~0.5 ug/L or ug/kg
USEPA Method 353.1/353.2/Hach 8507	Nitrogen, Nitrate-Nitrite (Colorimetric, Automated, Hydrazine Reduction) - Approved for NPDES and SDWA (Reissued w/Rev. 1978)	Nitrate, nitrite	Spectrophotometer	Laboratory/Field	No	0.01 mg/L
ASTM D1498 with commercially available ORP	Standard Practice for Oxidation-Reduction Potential of Water	Oxidation-reduction potential	ORP instrument	Field	No	
Hach 8146	Iron, Ferrous Method 8146 DR/2500.	Ferrous iron	Hach system	Field	No	0.02 mg/L
Hach 8034	Manganese Method 8034 WAH, DR/4000, DR/2500, DR/2400, or Genesys	Manganese	Hach system	Field	No	0.2 mg/L
Hach 8131	Sulfide Method 8131 WAH, DR/4000, DR/2500, DR/2400, or Genesys	Sulfide	Hach system	Field	No	5 mg/L
Hach 8205	Carbon Dioxide Method 8205 WAH	CO_2	Hach system	Field	No	10 mg/L
USEPA Method 160.1	Residue, Filterable (Gravimetric, Dried at 180°C) - Approved for NPDES (Issued 1971)	TDS	Drying oven	Laboratory	No	10 mg/L
USEPA Method 160.2	Residue, Non-Filterable (Gravimetric, Dried at 103-105°C) - Approved for NPDES (Issued 1971)	TSS	Drying Oven	Laboratory	No	4 mg/L
USEPA Method 350.3/HACH 8038/8155	Nitrogen, Ammonia (Potentiometric, Ion Selective Electrode) - Approved for NPDES (Issued 1974)	Ammonia	Ion selective electrode/	Laboratory/Field	No	0.03 mg/L
SW846 Section 7.3	Reactivity	Reactivity	Depending on sample characteristic	Laboratory	No	Depending on sample characteristic

Note: 1. Method quantitation limit listed by the method. Method reporting limit provided by the laboratory will be reviewed for each specific project.

Table 4
SUMMARY OF DEFINITIVE ANALYTICAL METHODS

Reference Number	Title, Revision Date, and/or Number	Analytical Group	Instrument
CLP OLC03.2/ASP2000	CLP Statement of Work (SOW) for Low Concentration Organic Analysis, OLC03.2 and NYSDEC (2000) ASP	Aqueous low concentration for VOCs, SVOCs, pesticides, and PCBs.	GC/MS (VOCs/SVOCs), GC/ECD (pesticides/PCBs)
CLP OLM04.3/ASP2000	CLP Statement of Work for Multi-Media, Multi-Concentration Organics Analysis, OLM04.3 and NYSDEC (2000) ASP.	VOCs, SVOCs, pesticides, PCBs	GC/MS (VOCs/SVOCs), GC/ECD (pesticides/PCBs)
SW846 Method 8260B	Volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS), Revision 2, 1996	Volatile organic compounds	GC/MS
SW846 Method 8270C	Semivolatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, 1998	Semivolatile Organic Compounds	GC/MS
SW846 Method 8081A/B	Organochlorine Pesticides By Gas Chromatography	Pesticides	GC
SW846 Method 8082A	Polychlorinated Biphenyls (PCBs) By Gas Chromatography	PCBs	GC
SW846 Method 6010B	Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 2, 1996	Metals	ICP/AES
SW846 Method 7471A	Mercury In Solid Or Semisolid Waste (Manual Cold-Vapor Technique), Revision 1, 1994	Mercury	Atomic absorption spectrophotometer
SW846 Method 9012A	Total And Amenable Cyanide (Automated Colorimeteric,With Off-line Distillation), Revision 1, 1996	Cyanide	Colorimeter
SW846 Method 8330	Nitroaromatics And Nitramines By High Performance Liquid Chromatography (HPLC), Revision 0, 1994	Nitroaromatics And Nitramines	HPLC
CLP ILM06.X/ASP2000	CLP Statement of Work for Multi-Media, Multi-Concentration Inorganic Analysis, ILM06.X and NYSDEC (2000) ASP	Metals and cyanide	ICP/AES or ICP/MS, AA (mercury), Spectrophotometer (cyanide)
SW846 Method 7580A	White Phosphorus (P) By Solvent Extraction And Gas Chromatography, Revision 0, 1990	White Phosphorus	Gas chromatograph
USEPA Method 314.0	Determination Of Perchlorate In Drinking Water Using Ion Chromatography, Revision 1.0, 1999	Perchlorate	Ion Chromatograph
SW846 Method 7196A	Chromium, Hexavalent (Colorimetric), Revision 1, 1992	Hexavalent chromium	Spectrophotometer or filter photometer
USEPA Method 335.2	Cyanide, Total (Titrimetric; Spectrophotometric) - Approved for NPDES (Technical Revision 1980)	Total cyanide	Spectrophotometer
USEPA Method 365.1/365.2	Phosphorous, All Forms (Colorimetric, Ascorbic Acid, Single Reagent) Approved for NPDES (1971)	Total phosphorus	Spectrophotometer
Method 418.1	Petroleum Hydrocarbons (Infrared Spectrophotometric)	Total Petroleum Hydrocarbons	Spectrophotometric, Infrared
USEPA 351.2 / SM4500	Determination of Total Kjeldahl Nitrogen by Semi-Automated Colorimetry	Total Kjeldahl Nitrogen (TKN)	Colorimeter

Table 4
SUMMARY OF DEFINITIVE ANALYTICAL METHODS

Reference Number	Title, Revision Date, and/or Number	Analytical Group	Instrument
RSK-175, USEPA Method 8015D, or AM20GAX	Analysis of Dissolved Methane, Ethane, and Ethylene in Groundwater by a Standard Gas Chromatograph Technique; Nonhalogenated Organics Using GC/FID, Revision4, 2003; Analytical Method AM20GAX Standard Operating Procedure for the Analysis of Biodegration Indicator Gases	Methane, Ethane, Ethene	Gas chromatograph/flame ionization detector GC/FID/TCD/RGD
SW846 Method 9060A/USEPA Method 415.1/Lloyd Kahn	Total Organic Carbon, Revision 1, 2002 Organic Carbon, Total (Combustion Or Oxidation) - Approved for NPDES (Editorial Revision 1974) Determination of Total Organic Carbon in Sediment, Lloyd Kahn, 1988	Total Organic Carbon	carbonaceous analyzer
USEPA Method 410.1	Chemical Oxygen Demand (Titrimetric, Mid-Level) - Approved for NPDES (Editorial Revision 1978)	Chemical Oxygen Demand	
USEPA Method 300.1 / USEPA Method 300.2 / SW846 Method 9056	Determination Of Inorganic Anions In Drinking Water By Ion Chromatography, Revision 1, 1999. Determination Of Inorganic Anions By Ion Chromatography, Revision 0, 1994	Nitrate, nitrite, chloride, sulfate	Ion Chromatography
UEPA Method 405.1	Biochemical Oxygen Demand (5 Days, 20°C) - Approved for NPDES (Editorial Revision 1974)	BOD	Oxygen probe
SW846 Method 1311 followed by 8260B	Toxicity Characteristic Leaching Procedure; Volatile Organic Compounds By Gas Chromatography/ Mass Spectrometry (GC/MS)	TCLP VOCs	GC/MS
SW846 Method 1311 followed by 8270C	Toxicity Characteristic Leaching Procedure; Semivolatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS)	TCLP SVOCs	GC/MS
SW846 Method 1311 followed by 8081B	Toxicity Characteristic Leaching Procedure; Organochlorine Pesticides By Gas Chromatography	TCLP pesticides	GC
SW846 Method 1311 followed by 8082A	Toxicity Characteristic Leaching Procedure; Polychlorinated Biphenyls (PCBs) By Gas Chromatography	TCLP PCBs	GC
SW846 Method 1311 followed by 8151A	Toxicity Characteristic Leaching Procedure; Chlorinated Herbicides By GC Using Methylation Or Pentafluorobenzylation Derivatization	TCLP herbicides	GC
SW846 Method 1311 followed by 6010B or 6020A	Toxicity Characteristic Leaching Procedure; Inductively Coupled Plasma –Atomic Emission Spectrometry; or Inductively Coupled Plasma – Mass Spectrometry	TCLP metals	AES or MS
40CFR261.23	Characteristic of Reactivity	Reactivity	
SW846 Method 1010A, ASTM D93-79, D93-80, or D3278-78	Pensky-Martens Closed-Cup Method For Determining Ignitability	Flashpoint	Pensky-Martens closed-cup tester
SW846 Method 9040C	pH Electrometric Measurement	pH	pH meter

Notes:

1) The above reference methods are from the following literatures:
   a) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (USEPA SW-846, Third Edition) and its subsequent updates.
   b) Methods for Chemical Analysis of Water and Waste (USEPA, 1979).
2) All definitive analyses will be conducted by selected laboratory. The laboratory should conduct the analyses in accordance with all NYSDEC ASP requirements and requirements specified in this ASP.

Table 5-A

Sample Containers, Preservatives, and Holding Times for Soils and Sediments

Parameter	Sample Container	Preservative	Technical Holding Time [1]	Laboratory Holding Time [2]
Metals	1 4 oz wide-mouth glass w/ Teflon-lined cap	Ice, Cool to 4°C	28 days (Hg); 24 hours (hex chromium); 14 days (cyanide); 180 days (others)	26 days (Hg); 24 hours (hex chromium)[d]; 12 days (cyanide), 178 days (others)
Explosives	1 4 oz wide-mouth glass w/ Teflon-lined cap	Ice, Cool to 4°C	7/40 days[a]	5/40 days[a]
Perchlorate	1 4 oz wide-mouth glass w/ Teflon-lined cap	Ice, Cool to 4°C	28 days	26 days
SVOCs	1 4 oz wide-mouth glass w/ Teflon-lined cap	Ice, Cool to 4°C	7/40 days[a]	5/40 days[a]
Pesticides/PCBs	1 4 oz wide-mouth glass w/ Teflon-lined cap	Ice, Cool to 4°C	7/40 days[a]	5/40 days[a]
VOCs (low level)	3 Encore samplers	Ice, Cool to 4°C	14 days	Preserve within 24 hours and analyze within 12 days
VOCs (medium or high level)	1 4 oz wide-mouth glass w/ Teflon-lined cap	Methanol, Ice, Cool to 4°C or preserve at the laboratory	10 days	8 days
TOC	1 4 oz wide-mouth glass w/ Teflon-lined cap	Ice, Cool to 4°C	14 days	12 days
Total Kjeldahl Nitrogen (TKN)	1 500 mL plastic or glass bottle	Ice, Cool to 4°C	28 days	26 days
Total Cyanide	1 500 mL plastic or glass bottle	Ice, Cool to 4°C	14 days	12 days
Iorn, Phosphorus, Potassium	1 4oz glass jar	Ice, Cool to 4°C	Iron and potassium - 180 days Phosphorus – 28 days	Iron and potassium - 178 days Phosphorus – 26 days
TCLP VOC	1 8 oz wide mouth glass with Teflon-lined cap	Ice, Cool to 4°C	14/NA/14[b]	7/NA/7[b]
TCLP SVOC	1 8 oz wide mouth glass with Teflon-lined cap	Ice, Cool to 4°C	14/7/40 [b]	5/7/40 [b]
TCLP Mercury	1 8 oz wide mouth glass with Teflon-lined cap	Ice, Cool to 4°C	28/NA/28 (mercury) [b]	5/NA/28 (mercury) [b]

Table 5-A

Sample Containers, Preservatives, and Holding Times for Soils and Sediments

Parameter	Sample Container	Preservative	Technical Holding Time [1]	Laboratory Holding Time [2]
TCLP Metals (except Mercury)	1 8 oz wide mouth glass with Teflon-lined cap	Ice, Cool to 4°C	180/NA/180 [b]	178/NA/180 [b]
Reactivity	2 4-oz plastic jar	Ice, Cool to 4°C	7	5
Flashpoint	1 100 ml plastic or glass bottle	Ice, Cool to 4°C	7	5
pH	1 4-oz plastic jar	Ice, Cool to 4°C	ASAP	ASAP

Notes:

1. Technical holding time between sample collection and sample analysis. Based on Region 2 SOPs, NYSDEC (2000) ASP, and method requirements.

2. Laboratory holding time requirement to meet technical holding time requirement. Holding time from Verified Time of Sample Receipt (VTSR) at the laboratory. Based on NYSDEC (2000) ASP and technical holding time requirement.

[a] number of days between sample collection and extraction / number of days between extraction and analysis;

[b] number of days between sample collection and TCLP extraction/number of days between TCLP extraction and preparative extraction/number of days between preparative extraction and analysis.

[c] TCLP SVOCs includes all semivolatiles, pesticides, and herbicides.

[d] Meet the laboratory holding time requirement does not automatically meet the technical holding time requirement. Special arrangement needed to meet the technical holding time requirement.

Table 5-B

Sample Containers, Preservatives, and Holding Times for Aqueous Samples

Parameter	Sample Container	Preservative	Technical Holding Time [1]	Laboratory Holding Time [2]
Metals	1 500-ml plastic bottle	pH<2, with HNO3, Ice, Cool to 4ºC	28 days (Hg); 24 hours (hex chromium); 180 days	26 days (Hg); 24 hours (hex chromium)[d]; 178 days
Explosives	2 1-L amber bottles	Ice, Cool to 4°C	7/40 days[a]	5/40 days[a]
Inorganic Ions	1 500-ml plastic bottle	Ice, Cool to 4°C	Nitrate, Nitrite - 48 hours Chloride, fluoride, sulfate – 28 days	Nitrate, Nitrite – 24 hours Chloride, fluoride, sulfate – 26 days
Perchlorate	1 250-ml plastic or glass bottle	Ice, Cool to 4°C	28 days	26 days
Alkalinity	1 250-ml plastic or glass bottle	Ice, Cool to 4°C	14 days	12 days
Total Cyanide	1 1L plastic or glass bottle	Ice, Cool to 4°C, NaOH to pH>12	14 days	12 days
Ammonia	1 500-ml plastic bottle	2 mL H_2SO_4 per liter, ice, cool to 4°C.	28 days	26 days
TSS, TDS	1 500-ml plastic bottle	Ice, cool to 4°C.	7 days	7 days
Hardness	1 100-ml plastic bottle	pH<2, with HNO3, Ice, Cool to 4ºC	6 months	178 days
SVOCs	2 1-L amber bottle	Ice, Cool to 4°C	7/40 days[a]	5/40 days[a]
Turbidity	1 500-ml plastic bottle	Ice, Cool to 4°C	48 hours	24 hours
TOC/COD	1 1-L amber bottle or 40-ml VOA vial for TOC	Ice, Cool to 4°C, with H_2SO_4 or HCl to pH<2	28 days	26 days
BOD	1 500-ml plastic bottle	Ice, Cool to 4°C	48 hours	24 hours
Pesticides	1 1-L amber bottle	Ice, Cool to 4°C	7/40 days[a]	5/40 days[a]
PCBs	1 1-L amber bottle	Ice, Cool to 4°C	7/40 days[a]	5/40 days[a]
VOCs	3 40 mL VOA vials	pH<2, with HCl, Ice , Cool to 4°C	14 days[a] (7 days if unpreserved)	10 days[a] (5 days if unpreserved)
Total Kjeldahl Nitrogen (TKN)	1 1-L amber bottle	Ice, Cool to 4°C, with H_2SO_4 to pH<2	28 days	26 days
MEE	1 60-ml serum bottle w/ Teflon-lined cap	Ice, Cool to 4°C, 4°C trisodium phosphate for Method AM20GAX	14 days[a]	12 days[a]
Total Petroleum Hydrocarbons	1 1-L glass bottle	pH<2, with HCl, Ice , Cool to 4°C	7/40 days[a]	5/40 days[a]

Table 5-B

Sample Containers, Preservatives, and Holding Times for Aqueous Samples

Parameter	Sample Container	Preservative	Technical Holding Time [1]	Laboratory Holding Time [2]
TCLP VOC	3 40 mL VOA vials	Ice, Cool to 4°C	14/NA/14[b]	7/NA/7[b]
TCLP SVOC [c]	1 1-L amber bottle	Ice, Cool to 4°C	14/7/40 [b]	5/7/40 [b]
TCLP Mercury	1 1-L amber bottle	Ice, Cool to 4°C	28/NA/28 [b]	5/NA/28 [b]
TCLP Metals (except Mercury)	1 1-L amber bottle	Ice, Cool to 4°C	180/NA/180 [b]	178/NA/180 [b]

Notes:

1. Technical holding time between sample collection and sample analysis. Based on Region 2 SOPs, NYSDEC (2000) ASP, and method requirements.

2. Laboratory holding time requirement to meet technical holding time requirement. Holding time from Verified Time of Sample Receipt (VTSR) at the laboratory. Based on NYSDEC (2000) ASP and technical holding time requirement.

[a] number of days between sample collection and extraction / number of days between extraction and analysis;

[b] number of days between sample collection and TCLP extraction/number of days between TCLP extraction and preparative extraction/number of days between preparative extraction and analysis.

[c] TCLP SVOCs includes all semivolatiles, pesticides, and herbicides.

[d] Meet the laboratory holding time requirement does not automatically meet the technical holding time requirement. Special arrangement needed to meet the technical holding time requirement.

Table 6-A

Target Analyte List and Project ARAR/TBC Limits[1] for Volatile Organic Compounds by GC/MS – Water

Volatile Organic Compound	CAS #	CRQL for CLP Low Concentration TCL (OLC03.2/ASP2000) [2] ug/L	CRQL for CLP Water TCL (CLP OLM04.3/ASP 2000) [3] ug/L	Groundwater ARAR/TBC Value [4] ug/L	Surface Water ARAR/TBC Value [5] ug/L
Dichlorodifluoromethane	75-71-8	0.5	10	5	
Chloromethane	74-87-3	0.5	10	5	
Bromomethane	74-83-9	0.5	10	5	
Vinyl chloride	75-01-4	0.5	10	2	
Chloroethane	75-00-3	0.5	10	5	
Trichlorofluoromethane	75-69-4	0.5	10	5	
1,1-Dichloroethene	75-35-4	0.5	10	5	
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	0.5	10	5	
Acetone	67-64-1	5.0	10	50	
Carbon Disulfide	75-15-0	0.5	10	60	
Methyl Acetate	79-20-9	0.5	10		
Methylene chloride	75-09-2	0.5	10	5	200 (H)
trans-1,2-Dichloroethene	156-60-5	0.5	10	5	
Methyl tert-Butyl Ether	1634-04-4	0.5	10	10	
1,1-Dichloroethane	75-35-3	0.5	10	5	
Cis-1,2-Dichloroethene	156-59-2	0.5	10	5	
2-Butanone	78-93-3	5.0	10	50	
Chloroform	67-66-3	0.5	10	7	
1,1,1-Trichloroethane	71-55-6	0.5	10	5	
Cyclohexane	110-82-7	0.5	10		
Carbon tetrachloride	56-23-5	0.5	10	5	
Benzene	71-43-2	0.5	10	1	210
1,2-Dichloroethane	107-06-2	0.5	10	0.6	
Trichloroethene	79-01-6	0.5	10	5	40 (H)
Methylcyclohexane	108-87-2	0.5	10		
1,2-Dichloropropane	78-87-5	0.5	10	1	
Bromodichloromethane	75-27-4	0.5	10	50	
Cis-1,3-Dichloropropene	10061-01-5	0.5	10	0.4 [6]	
4-Methyl-2-pentanone	108-10-1	5.0	10		
Toluene	108-88-3	0.5	10	5	100
trans-1,3-Dichloropropene	10061-02-6	0.5	10	0.4 [6]	
1,1,2-Trichloroethane	79-00-5	0.5	10	1	
Tetrachloroethene	127-18-4	0.5	10	5	1 (H)
2-Hexanone	591-78-6	5.0	10	50	

Table 6-A

Target Analyte List and Project ARAR/TBC Limits[1] for Volatile Organic Compounds by GC/MS – Water

Volatile Organic Compound	CAS #	CRQL for CLP Low Concentration TCL (OLC03.2/ASP2000) [2] ug/L	CRQL for CLP Water TCL (CLP OLM04.3/ASP 2000) [3] ug/L	Groundwater ARAR/TBC Value [4] ug/L	Surface Water ARAR/TBC Value [5] ug/L
Dibromochloromethane	124-48-1	0.5	10	50	
1,2-Dibromoethane	106-93-4	0.5	10	0.0006	
Chlorobenzene	108-90-7	0.5	10	5	5
Ethyl Benzene	100-41-4	0.5	10	5	17
Total Xylenes	1330-20-7	0.5	10	5	65
Styrene	100-42-5	0.5	10	5	
Bromoform	75-25-2	0.5	10	50	
Isopropylbenzene	98-82-8	0.5	10	5	2.6
1,1,2,2-Tetrachloroethane	79-34-5	0.5	10	5	
1,3-Dichlorobenzene	541-73-1	0.5	10	3	5 [7]
1,4-Dichlorobenzene	106-46-7	0.5	10	3	5 [7]
1,2-Dichlorobenzene	95-50-1	0.5	10	3	5 [7]
1,2-Dibromo-3-chloropropane	96-12-8	0.5	10	0.04	
1,2,3-Trichlorobenzene	87-61-6	0.5	--	5	5 [8]
1,2,4-Trichlorobenzene	120-82-1	0.5	10	5	5 [8]
Bromochloromethane	74-97-5	0.5	--	5	

Notes:
1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. From CLP SOW for OLC03.2.
3. From CLP SOW for OLM04.3.
4. MCL, Secondary Drinking Water Regulations, or NYSDEC TOGS 1.1.1 for Class GA water, whichever is lower.
5. NYSDEC TOGS 1.1.1 for Class C water, or AWQC (USEPA, 2004) Criterion Continuous Concentration, whichever is lower. NYSDEC standards/guidelines for fresh water fish survival/propagation and wildlife protection were used; when not available, other standards/guidelines (human consumption of fish and aesthetic) were used.
   H – Human consumption of fish.
6. 0.4 ug/L applies to the sum of cis- and trans-1,3-dichloropropene.
7. Applies to the sum of 1,2-, 1,3- and 1,4-dichlorobenzene.
8. Applies to the sum of 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene.
-- Not on the CLP Low Concentration Organics TCL or CLP TCL.

Table 6-B

Target Analyte List and Project ARAR/TBC Limits[1] for Volatile Organic Compounds by GC/MS – Soil and Sediment

Volatile Organic Compound	CAS #	CRQL for CLP (CLP OLM04.3/ASP 2000) TCL [2] - Low Soil ug/kg	CRQL for CLP (CLP OLM04.3/ASP 2000) TCL [2] – Medium Soil ug/kg	NYSDEC TAGM [3] ug/kg	NYSDEC Sediment Screening Value [4] ug/kg
Dichlorodifluoromethane	75-71-8	10	1200		
Chloromethane	74-87-3	10	1200		
Bromomethane	74-83-9	10	1200		
Vinyl chloride	75-01-4	10	1200	200	
Chloroethane	75-00-3	10	1200	1900	
Trichlorofluoromethane	75-69-4	10	1200		
1,1-Dichloroethene	75-35-4	10	1200	400	
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	10	1200	6000	
Acetone	67-64-1	10	1200	200	
Carbon Disulfide	75-15-0	10	1200	2700	
Methyl Acetate	79-20-9	10	1200		
Methylene chloride	75-09-2	10	1200	100	
trans-1,2-Dichloroethene	156-60-5	10	1200	300	
Methyl tert-Butyl Ether	1634-04-4	10	1200		
1,1-Dichloroethane	75-35-3	10	1200	200	
Cis-1,2-Dichloroethene	156-59-2	10	1200		
2-Butanone	78-93-3	10	1200	300	
Chloroform	67-66-3	10	1200	300	
1,1,1-Trichloroethane	71-55-6	10	1200	800	
Cyclohexane	110-82-7	10	1200		
Carbon tetrachloride	56-23-5	10	1200	600	
Benzene	71-43-2	10	1200	60	280
1,2-Dichloroethane	107-06-2	10	1200	100	
Trichloroethene	79-01-6	10	1200	700	
Methylcyclohexane	108-87-2	10	1200		
1,2-Dichloropropane	78-87-5	10	1200		
Bromodichloromethane	75-27-4	10	1200		
Cis-1,3-Dichloropropene	10061-01-5	10	1200		
4-Methyl-2-pentanone	108-10-1	10	1200	1000	
Toluene	108-88-3	10	1200	1500	490
trans-1,3-Dichloropropene	10061-02-6	10	1200		
1,1,2-Trichloroethane	79-00-5	10	1200		

Table 6-B

Target Analyte List and Project ARAR/TBC Limits[1] for Volatile Organic Compounds by GC/MS – Soil and Sediment

Volatile Organic Compound	CAS #	CRQL for CLP (CLP OLM04.3/ASP 2000) TCL [2] - Low Soil ug/kg	CRQL for CLP (CLP OLM04.3/ASP 2000) TCL [2] – Medium Soil ug/kg	NYSDEC TAGM [3] ug/kg	NYSDEC Sediment Screening Value [4] ug/kg
Tetrachloroethene	127-18-4	10	1200	1400	
2-Hexanone	591-78-6	10	1200		
Dibromochloromethane	124-48-1	10	1200		
1,2-Dibromoethane	106-93-4	10	1200		
Chlorobenzene	108-90-7	10	1200	1700	35
Ethyl Benzene	100-41-4	10	1200	5500	240
Total Xylenes	1330-20-7	10	1200	1200	920
Styrene	100-42-5	10	1200		
Bromoform	75-25-2	10	1200		
Isopropylbenzene	98-82-8	10	1200		120
1,1,2,2-Tetrachloroethane	79-34-5	10	1200	600	
1,3-Dichlorobenzene	541-73-1	10	1200	1600	120 [5]
1,4-Dichlorobenzene	106-46-7	10	1200	8500	120 [5]
1,2-Dichlorobenzene	95-50-1	10	1200	7900	120 [5]
1,2-Dibromo-3-chloropropane	96-12-8	10	1200		
1,2,4-Trichlorobenzene	120-82-1	10	1200	3400	910 [6]

Notes:
1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. From CLP SOW for OLM04.3. The CRQLs for soil are based on 100% solids. Samples with less than 100% solids may have CRQLs greater than those listed in the table above.
3. From NYSDEC TAGM #4046.
4. From NYSDEC (1999) Technical Guidance for Screening Contaminated Sediments. Benthic aquatic life chronic toxicity for freshwater sediment was used and sediment was assumed to contain 1% organic carbon.
5. For dichlorobenzenes.
6. For trichlorobenzenes.
-- Not on the CLP Low Concentration Organics TCL or CLP TCL.

Table 6-C

Target Analyte List and Project ARAR/TBC Limits[1] for Semivolatile Organic Compounds by GC/MS – Water

Semivolatile Compound	CAS #	CLP OLC03.2 CRQL [2] ug/L	CLP OLM04.3 CRQL [3] ug/L	Groundwater ARAR/TBC Value [4] ug/L	Surface Water ARAR/TBC [5] ug/L
Benzaldehyde	100-52-7	5.0	10		
Phenol	108-95-2	5.0	10	1 [6]	5.0 [7]
bis(2-Chloroethyl) ether	111-44-4	5.0	10	1.0	
2-Chlorophenol	95-57-8	5.0	10	1 [6]	1.0 [8]
2-Methylphenol	95-48-7	5.0	10	1 [6]	5.0 [7]
2,2'-oxybis(1-Chloro-propane)	108-60-1	5.0	10	5	
Acetophenone	98-86-2	5.0	10		
4-Methylphenol	106-44-5	5.0	10	1 [6]	5.0 [7]
N-Nitroso-di-n-propylamine	621-64-7	5.0	10		
Hexachloroethane	67-72-1	5.0	10	5	0.6 (H)
Nitrobenzene	98-95-3	5.0	10	0.4	
Isophorone	78-59-1	5.0	10	50	
2-Nitrophenol	88-75-5	5.0	10	1	5.0 [7]
2,4-Dimethylphenol	105-67-9	5.0	10	50	5.0 [7]
bis(2-Chloroethoxy)methane	111-91-1	5.0	10	5	
2,4-Dichlorophenol	120-83-2	5.0	10	5	1.0 [8]
1,2,4-Trichlorobenzene	120-82-1	--	10	5	5
Naphthalene	91-20-3	5.0	10	10	13
4-Chloroaniline	106-47-8	5.0	10	5	
Hexachlorobutadiene	87-68-3	5.0	10	0.5	1.0
Caprolactam	105-60-2	5.0	10		
4-Chloro-3-methylphenol	59-50-7	5.0	10	1 [6]	1.0 [8]
2-Methylnaphthalene	91-57-6	5.0	10		4.7
Hexachlorocyclopentadiene	77-47-4	5.0	10	5	0.45
2,4,6-Trichlorophenol	88-06-2	5.0	10	1 [6]	1.0 [8]
2,4,5-Trichlorophenol	95-95-4	20	25	1 [6]	1.0 [8]
1,1'-Biphenyl	92-52-4	5.0	10	5	
2-Chloronaphthalene	91-58-7	5.0	10	10	
2-Nitroaniline	88-74-4	20	25	5	
Dimethyl phthalate	131-11-3	5.0	10	50	
Acenaphthylene	208-96-8	5.0	10		
2,6-Dinitrotoluene	606-20-2	5.0	10	5	
3-Nitroaniline	99-09-2	20	25	5	
Acenaphthene	83-32-9	5.0	10	20	5.3
2,4-Dinitrophenol	51-28-5	20	25	10	5.0 [7]
4-Nitrophenol	100-02-7	20	25	1 [6]	5.0 [7]
Dibenzofuran	132-64-9	5.0	10		
2,4-Dinitrotoluene	121-14-2	5.0	10	5	

Table 6-C

Target Analyte List and Project ARAR/TBC Limits[1] for Semivolatile Organic Compounds by GC/MS – Water

Semivolatile Compound	CAS #	CLP OLC03.2 CRQL [2] ug/L	CLP OLM04.3 CRQL [3] ug/L	Groundwater ARAR/TBC Value [4] ug/L	Surface Water ARAR/TBC [5] ug/L
Diethylphthalate	84-66-2	5.0	10	50	
4-Chlorophenyl phenyl ether	7005-72-3	5.0	10		
Fluorene	86-73-7	5.0	10	50	0.54
4-Nitroaniline	100-01-6	20	25	5	
4,6-Dinitro-2-methylphenol	534-52-1	20	25	1 [6]	5.0 [7]
N-nitrosodiphenylamine	86-30-6	5.0	10	50	
1,2,4,5-Tetrachlorobenzene	95-94-3	5.0	--	5	
4-Bromophenyl phenyl ether	101-55-3	5.0	10		
Hexachlorobenzene	118-74-1	5.0	10	0.04	$3x10^{-5}$ (H)
Atrazine	1912-24-9	5.0	10	3	
Pentachlorophenol	87-86-5	20	25	1 [6]	1.0 [8]
Phenanthrene	85-01-8	5.0	10	50	5.0
Anthracene	120-12-7	5.0	10	50	3.8
Carbazole	86-74-8	--	10		
Di-n-butyl phthalate	84-74-2	5.0	10	50	
Fluoranthene	206-44-0	5.0	10	50	
Pyrene	129-00-0	5.0	10	50	4.6
Butyl benzyl phthalate	85-68-7	5.0	10	50	
3,3'-Dichlorobenzidine	91-94-1	5.0	10	5	
Benz[a]anthracene	56-55-3	5.0	10	0.002	0.03
Chrysene	218-01-9	5.0	10	0.002	
bis(2-Ethylhexyl)phthalate	117-81-7	5.0	10	5	0.6
Di-n-octyl phthalate	117-84-0	5.0	10	50	
Benzo[b]fluoranthene	205-99-2	5.0	10	0.002	
Benzo[k]fluoranthene	207-08-9	5.0	10	0.002	
Benzo[a]pyrene	50-32-8	5.0	10	ND (MCL=0.2)	0.0012 (H)
Indeno(1,2,3-cd]pyrene	193-39-5	5.0	10	0.002	
Dibenz[a,h]anthracene	53-70-3	5.0	10		
Benzo[g,h,i]perylene	191-24-2	5.0	10		

Notes:
1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. From CLP SOW for OLC03.2.
3. From CLP SOW for OLM04.3.
4. MCL, Secondary Drinking Water Regulations, or NYSDEC TOGS 1.1.1 for Class GA water, whichever is lower.
5. NYSDEC TOGS 1.1.1 for Class C water, or AWQC (USEPA, 2004) Criterion Continuous Concentration, whichever is lower. NYSDEC standards/guidelines for fresh water fish survival/propagation and wildlife protection were used; when not available, other standards/guidelines (human consumption of fish and aesthetic) were used.
H – Human consumption of fish.
6. For total phenols.
7. For total unchlorinated phenols.
8. For total chlorinated phenols.
-- Not on the CLP Low Concentration Organics TCL or CLP TCL.

Table 6-D

Target Analyte List and Project ARAR/TBC Limits[1] for Semivolatile Organic Compounds by GC/MS – Soil and Sediment

Semivolatile Compound	CAS #	CLP OLM04.3 CRQL [2] - Low Soil ug/kg	CLP OLM04.3 CRQL [2] – Medium Soil ug/kg	NYSDEC TAGM [3] ug/kg	NYSDEC Sediment Screening Value [4] ug/kg
Benzaldehyde	100-52-7	330	10000		
Phenol	108-95-2	330	10000	30	
bis(2-Chloroethyl) ether	111-44-4	330	10000		
2-Chlorophenol	95-57-8	330	10000	800	
2-Methylphenol	95-48-7	330	10000	100	
2,2'-oxybis(1-Chloro-propane)	108-60-1	330	10000		
Acetophenone	98-86-2	330	10000		
4-Methylphenol	106-44-5	330	10000	900	
N-Nitroso-di-n-propylamine	621-64-7	330	10000		
Hexachloroethane	67-72-1	330	10000		
Nitrobenzene	98-95-3	330	10000	200	
Isophorone	78-59-1	330	10000	4400	
2-Nitrophenol	88-75-5	330	10000	330	
2,4-Dimethylphenol	105-67-9	330	10000		
bis(2-Chloroethoxy)methane	111-91-1	330	10000		
2,4-Dichlorophenol	120-83-2	330	10000	400	
1,2,4-Trichlorobenzene	120-82-1	330	10000	3400	
Naphthalene	91-20-3	330	10000	13000	
4-Chloroaniline	106-47-8	330	10000	220	
Hexachlorobutadiene	87-68-3	330	10000		55
Caprolactam	105-60-2	330	10000		
4-Chloro-3-methylphenol	59-50-7	330	10000	240	
2-Methylnaphthalene	91-57-6	330	10000	36400	
Hexachlorocyclopentadiene	77-47-4	330	10000		44
2,4,6-Trichlorophenol	88-06-2	330	10000		
2,4,5-Trichlorophenol	95-95-4	800	25000	100	
1,1'-Biphenyl	92-52-4	330	10000		
2-Chloronaphthalene	91-58-7	330	10000		
2-Nitroaniline	88-74-4	800	25000	430	
Dimethyl phthalate	131-11-3	330	10000	2000	
Acenaphthylene	208-96-8	330	10000	41000	
2,6-Dinitrotoluene	606-20-2	330	10000	1000	
3-Nitroaniline	99-09-2	800	25000	500	
Acenaphthene	83-32-9	330	10000	50000	1400
2,4-Dinitrophenol	51-28-5	800	25000	200	
4-Nitrophenol	100-02-7	800	25000	100	
Dibenzofuran	132-64-9	330	10000	6200	

Table 6-D

Target Analyte List and Project ARAR/TBC Limits[1] for Semivolatile Organic Compounds by GC/MS – Soil and Sediment

Semivolatile Compound	CAS #	CLP OLM04.3 CRQL [2] - Low Soil ug/kg	CLP OLM04.3 CRQL [2] – Medium Soil ug/kg	NYSDEC TAGM [3] ug/kg	NYSDEC Sediment Screening Value [4] ug/kg
2,4-Dinitrotoluene	121-14-2	330	10000		
Diethylphthalate	84-66-2	330	10000	7100	
4-Chlorophenyl phenyl ether	7005-72-3	330	10000		
Fluorene	86-73-7	330	10000	50000	
4-Nitroaniline	100-01-6	800	25000		
4,6-Dinitro-2-methylphenol	534-52-1	800	25000		
N-nitrosodiphenylamine	86-30-6	330	10000		
4-Bromophenyl phenyl ether	101-55-3	330	10000		
Hexachlorobenzene	118-74-1	330	10000	410	55700
Atrazine	1912-24-9	330	10000		
Pentachlorophenol	87-86-5	800	25000	1000	
Phenanthrene	85-01-8	330	10000	50000	
Anthracene	120-12-7	330	10000	50000	
Carbazole	86-74-8	330	10000		
Di-n-butyl phthalate	84-74-2	330	10000	8100	
Fluoranthene	206-44-0	330	10000	50000	
Pyrene	129-00-0	330	10000	50000	
Butyl benzyl phthalate	85-68-7	330	10000	50000	
3,3'-Dichlorobenzidine	91-94-1	330	10000		
Benz[a]anthracene	56-55-3	330	10000	224	
Chrysene	218-01-9	330	10000	400	
bis(2-Ethylhexyl)phthalate	117-81-7	330	10000	50000	1995
Di-n-octyl phthalate	117-84-0	330	10000	50000	
Benzo[b]fluoranthene	205-99-2	330	10000	1100	
Benzo[k]fluoranthene	207-08-9	330	10000	1100	
Benzo[a]pyrene	50-32-8	330	10000	61	
Indeno(1,2,3-cd]pyrene	193-39-5	330	10000	3200	
Dibenz[a,h]anthracene	53-70-3	330	10000	14	
Benzo[g,h,i]perylene	191-24-2	330	10000	50000	

Notes:
1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. From CLP SOW for OLM04.3. The CRQLs for soil are based on 100% solids. Samples with less than 100% solids may have CRQLs greater than those listed in the table above.
3. From NYSDEC TAGM #4046.
4. From NYSDEC (1999) Technical Guidance for Screening Contaminated Sediments. Benthic aquatic life chronic toxicity for freshwater sediment was used and sediment was assumed to contain 1% organic carbon.
5. For dichlorobenzenes.
6. For trichlorobenzenes.
-- Not on the CLP Low Concentration Organics TCL or CLP TCL.

Table 6-E

Target Analyte List and Project ARAR/TBC Limits[1] for Explosives by HPLC - Water

Explosive Compound	CAS #	Groundwater ARAR/TBC Value [4] ug/L	Surface Water ARAR/TBC Value [5] ug/L
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	2691-41-0		
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4		
1,3,5-Trinitrobenzene	99-35-4	5	
1,3-Dinitrobenzene	99-65-0	5	
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)	479-45-8		
Nitrobenzene	98-95-3	0.4	
2,4,6-Trinitrotoluene (TNT)	118-96-7	5	
4-Amino-2,6-dinitrotoluene	19406-51-0		
2-Amino-4,6-dinitrotoluene	35572-78-2		
2,4-Dinitrotoluene	121-14-2	5	
2,6-Dinitrotoluene	606-20-2	5	
2-Nitrotoluene	88-72-2	5	
3-Nitrotoluene	99-08-1	5	
4-Nitrotoluene	99-99-0	5	
Nitroglycerin [2]	55-63-0		
Pentaerythritol Tetranitrate [3]	78-11-5		

Notes:

1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project. TALs based on SW-846 Method 8330.
2. Requires SW8332 or modification to SW8330; modification must be identified in SOP.
3. Requires modification to SW8330; modification must be identified in SOP.
4. MCL, Secondary Drinking Water Regulations, or NYSDEC TOGS 1.1.1 for Class GA water, whichever is lower.
5. NYSDEC TOGS 1.1.1 for Class C water, or AWQC (USEPA, 2004) Criterion Continuous Concentration, whichever is lower. NYSDEC standards/guidelines for fresh water fish survival/propagation and wildlife protection were used; when not available, other standards/guidelines (human consumption of fish and aesthetic) were used.
   H – Human consumption of fish.

Table 6-F

Target Analyte List and Project ARAR/TBC Limits[1] for Explosives by HPLC – Soil and Sediment

Explosive Compound	CAS #	NYSDEC TAGM [4] ug/kg	NYSDEC Sediment Screening Value [5] ug/kg
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	2691-41-0		
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4		
1,3,5-Trinitrobenzene	99-35-4		
1,3-Dinitrobenzene	99-65-0		
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)	479-45-8		
Nitrobenzene	98-95-3	200	
2,4,6-Trinitrotoluene (TNT)	118-96-7		
4-Amino-2,6-dinitrotoluene	19406-51-0		
2-Amino-4,6-dinitrotoluene	35572-78-2		
2,4-Dinitrotoluene	121-14-2		
2,6-Dinitrotoluene	606-20-2	1000	
2-Nitrotoluene	88-72-2		
3-Nitrotoluene	99-08-1		
4-Nitrotoluene	99-99-0		
Nitroglycerin [2]	55-63-0		
Pentaerythritol Tetranitrate [3]	78-11-5		

Notes:

1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project. TALs based on SW-846 Method 8330. The CRQLs for soil are based on 100% solids. Samples with less than 100% solids may have CRQLs greater than those listed in the table above.
2. Requires SW8332 or modification to SW8330; modification must be identified in SOP.
3. Requires modification to SW8330; modification must be identified in SOP.
4. From NYSDEC TAGM #4046.
5. From NYSDEC (1999) Technical Guidance for Screening Contaminated Sediments. Benthic aquatic life chronic toxicity for freshwater sediment was used and sediment was assumed to contain 1% organic carbon.

Table 6-G

Target Analyte List and Project ARAR/TBC Limits[1] for Organochlorine Pesticides by GC/ECD – Water

Organochlorine Pesticide Compound	CAS #	CRQL for CLP Low Concentration TCL (OLC03.2/ASP 2000) [2] ug/L	CRQL for CLP Water TCL (CLP OLM04.3/ASP 2000) [3] ug/L	Groundwater ARAR/TBC Value [4] ug/L	Surface Water ARAR/TBC Value [5] ug/L
Alpha-BHC	319-84-6	0.01	0.050	0.01	0.002
Beta-BHC	319-85-7	0.01	0.050	0.04	0.007
Delta-BHC	319-86-8	0.01	0.050	0.04	0.008
gamma-BHC (Lindane)	58-89-9	0.01	0.050	0.05	0.95
Heptachlor	76-44-8	0.01	0.050	0.04	$2x10^{-4}$ (H)
Aldrin	309-00-2	0.01	0.050	ND	0.001 (H)[6]
Heptachlor epoxide	1024-57-3	0.01	0.050	0.03	$3x10^{-4}$ (H)
Endosulfan I	959-98-8	0.01	0.050		
Dieldrin	60-57-1	0.02	0.10	0.004	0.056
4,4'-DDE	72-55-9	0.02	0.10	0.2	$1.1x10^{-5}$ [7]
Endrin	72-20-8	0.02	0.10	ND (MCL=2)	0.036
Endosulfan II	33213-65-9	0.02	0.10		
4,4'-DDD	72-54-8	0.02	0.10	0.3	$1.1x10^{-5}$ [7]
Endosulfan sulfate	1031-07-8	0.02	0.10		
4,4'-DDT	50-29-3	0.02	0.10	0.2	$1.1x10^{-5}$ [7]
Methoxychlor	72-43-5	0.10	0.50	35	0.03
Endrin ketone	53494-70-5	0.02	0.10	5	
Endrin aldehyde	7421-36-3	0.02	0.10		
Alpha-Chlordane	5103-71-9	0.01	0.050	2 [8]	
gamma-Chlordane	5103-74-2	0.01	0.050	2 [8]	
Toxaphene	8001-35-2	1.0	5.0	0.06	0.005

Notes:
1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. From CLP SOW for OLC03.2.
3. From CLP SOW for OLM04.3.
4. MCL, Secondary Drinking Water Regulations, or NYSDEC TOGS 1.1.1 for Class GA water, whichever is lower.
5. NYSDEC TOGS 1.1.1 for Class C water, or AWQC (USEPA, 2004) Criterion Continuous Concentration, whichever is lower. NYSDEC standards/guidelines for fresh water fish survival/propagation and wildlife protection were used; when not available, other standards/guidelines (human consumption of fish and aesthetic) were used.
H – Human consumption of fish.
6. Applies to the sum of aldrin and dieldrin.
7. Applies Applies to the sum of p,p'-DDD, p,p'-DDE and p,p'-DDT.
8. MCL for chlordane.
-- - Not on the CLP Low Concentration Organics TCL or CLP TCL.
ND – Not detected.

Table 6-H

Target Analyte List and Project ARAR/TBC Limits[1] for Organochlorine Pesticides by GC/ECD – Soil and Sediment

Organochlorine Pesticide Compound	CAS #	CRQL for CLP (CLP OLM04.3/ASP 2000) TCL [2] ug/kg	NYSDEC TAGM [3] ug/kg	NYSDEC Sediment Screening Value [4] ug/kg
alpha-BHC	319-84-6	1.7	110	0.6
beta-BHC	319-85-7	1.7	200	0.6
delta-BHC	319-86-8	1.7	300	0.6
gamma-BHC (Lindane)	58-89-9	1.7	60	0.6
Heptachlor	76-44-8	1.7	100	1
Aldrin	309-00-2	1.7	41	
Heptachlor epoxide	1024-57-3	1.7	20	1
Endosulfan I	959-98-8	1.7	900	0.3 [6]
Dieldrin	60-57-1	3.3	44	90
4,4'-DDE	72-55-9	3.3	2100	10
Endrin	72-20-8	3.3	100	40
Endosulfan II	33213-65-9	3.3	900	0.3 [6]
4,4'-DDD	72-54-8	3.3	2900	10
Endosulfan sulfate	1031-07-8	3.3	1000	0.3 [6]
4,4'-DDT	50-29-3	3.3	2100	10
Methoxychlor	72-43-5	17.0	10000	6
Endrin ketone	53494-70-5	3.3		40 [7]
Endrin aldehyde	7421-36-3	3.3		40 [7]
alpha-Chlordane	5103-71-9	1.7	540 [5]	0.3 [5]
gamma-Chlordane	5103-74-2	1.7	540 [5]	0.3 [5]
Toxaphene	8001-35-2	170.0		0.1

Notes:
1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. From CLP SOW for OLM04.3. The CRQLs for soil are based on 100% solids. Samples with less than 100% solids may have CRQLs greater than those listed in the table above.
3. From NYSDEC TAGM #4046.
4. From NYSDEC (1999) Technical Guidance for Screening Contaminated Sediments. Benthic aquatic life chronic toxicity for freshwater sediment was used and sediment was assumed to contain 1% organic carbon.
5. For chlordane.
6. For endosulfan.
7. For endrin.

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Table 6-I

Target Analyte List and Project ARAR/TBC Limits[1] for Polychlorinated Biphenyls by GC/ECD - Water

PCB Compound	CAS #	CRQL for CLP Low Concentration TCL (OLC03.2/ASP2000) [2] ug/L	CRQL for CLP Water TCL (CLP OLM04.3/ASP 2000) [3] ug/L	Groundwater ARAR/TBC Value [4] ug/L	Surface Water ARAR/TBC Value [5] ug/L
Aroclor 1016	12674-11-2	0.20	1.0	0.09 [6]	$1.2x10^{-4}$ [6]
Aroclor 1221	11104-28-2	0.20	2.0	0.09 [6]	1.2x10
Aroclor 1232	11141-16-5	0.40	1.0	0.09 [6]	1.2x10
Aroclor 1242	53469-21-9	0.20	1.0	0.09 [6]	1.2x10
Aroclor 1248	12672-29-6	0.20	1.0	0.09 [6]	1.2x10
Aroclor 1254	11097-69-1	0.20	1.0	0.09 [6]	1.2x10
Aroclor 1260	11096-82-5	0.20	1.0	0.09 [6]	1.2x10

Notes:
1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. From CLP SOW for OLC03.2.
3. From CLP SOW for OLM04.3.
4. MCL, Secondary Drinking Water Regulations, or NYSDEC TOGS 1.1.1 for Class GA water, whichever is lower.
5. NYSDEC TOGS 1.1.1 for Class C water, or AWQC (USEPA, 2004) Criterion Continuous Concentration, whichever is lower. NYSDEC standards/guidelines for fresh water fish survival/propagation and wildlife protection were used; when not available, other standards/guidelines (human consumption of fish and aesthetic) were used.
6. Applies to the sum of PCB compounds.

Table 6-J

Target Analyte List and Project ARAR/TBC Limits[1] for Polychlorinated Biphenyls by GC/ECD – Soil and Sediment

PCB Compound	CAS #	CRQL for CLP (CLP OLM04.3/ASP 2000) TCL [2] ug/kg	NYSDEC TAGM [3] ug/kg	NYSDEC Sediment Screening Value [4] ug/kg
Aroclor 1016	12674-11-2	33	1000 (surface) 10000 (subsurface)	193
Aroclor 1221	11104-28-2	67	1000 (surface) 10000 (subsurface)	193
Aroclor 1232	11141-16-5	33	1000 (surface) 10000 (subsurface)	193
Aroclor 1242	53469-21-9	33	1000 (surface) 10000 (subsurface)	193
Aroclor 1248	12672-29-6	33	1000 (surface) 10000 (subsurface)	193
Aroclor 1254	11097-69-1	33	1000 (surface) 10000 (subsurface)	193
Aroclor 1260	11096-82-5	33	1000 (surface) 10000 (subsurface)	193

Notes:
1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. From CLP SOW for OLM04.3. The CRQLs for soil are based on 100% solids. Samples with less than 100% solids may have CRQLs greater than those listed in the table above.
3. From NYSDEC TAGM #4046.
4. From NYSDEC (1999) Technical Guidance for Screening Contaminated Sediments. Benthic aquatic life chronic toxicity for freshwater sediment was used and sediment was assumed to contain 1% organic carbon.

Table 6-K

Target Analyte List and Project ARAR/TBC Limits[1] for Inorganics – Water

Metal	CAS #	Contract Required Quantitation Level for ICP-AES[2] (µg/L)	Contract Required Quantitation Level for ICP-MS[2] (µg/L)	Groundwater ARAR/TBC Value [3] ug/L	Surface Water ARAR/TBC Value [4] ug/L
Aluminum	7429-90-5	500	50	50	100
Antimony	7440-36-0	60	5	3	
Arsenic	7440-38-2	30	1	25	150
Barium	7440-39-3	50	5	1000	
Beryllium	7440-41-7	5	1	3	11 [5] 1100 [6]
Cadmium	7440-43-9	5	1	5	0.25
Calcium	7440-70-2	2000	200		
Chromium	7440-47-3	15	5	50	74 (Cr III) 11 (Cr VI)
Cobalt	7440-48-4	20	1		5
Copper	7440-50-8	25	5	200	9.0
Iron	7439-89-6	200	200	300 [7] 500 [8]	
Lead	7439-92-1	20	1	15	2.5
Magnesium	7439-95-4	1000	100	35000	
Manganese	7439-96-5	20	5	50	
Mercury	7439-97-6	0.5	--	0.7	0.0026
Nickel	7440-02-0	40	5	100	52
Potassium	7440-09-7	2000	200		
Selenium	7782-49-2	40	5	10	4.6
Silver	7440-22-4	15	1	50	0.1
Sodium	7440-23-5	3000	300	20000	
Thallium	7440-28-0	50	1	0.5	8
Vanadium	7440-62-2	25	5		14
Zinc	7440-66-6	75	10	2000	81
Cyanide	7440-67-7	20	--	200	1

Notes:

1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. From CLP SOW for ILM06.x.
3. MCL, Secondary Drinking Water Regulations, or NYSDEC TOGS 1.1.1 for Class GA water, whichever is lower.
4. NYSDEC TOGS 1.1.1 for Class C water, or AWQC (USEPA, 2004) Criterion Continuous Concentration, whichever is lower. NYSDEC standards/guidelines for fresh water fish survival/propagation and wildlife protection were used; when not available, other standards/guidelines (human consumption of fish and aesthetic) were used. A default hardness value of 100 ppm was assumed for ARAR/TBCs dependent on hardness.
5. When hardness is less than or equal to 75 ppm.
6. When hardness is greater than 75 ppm.
7. Applies for iron and manganese, respectively.
8. Applies to the sum of iron and manganese.

Table 6-L

Target Analyte List and Project ARAR/TBC Limits[1] for Inorganics – Soil and Sediment

Metal	CAS #	Contract Required Quantitation Level for ICP-AES[2] (mg/kg)	Contract Required Quantitation Level for ICP-MS[2] (mg/kg)	NYSDEC TAGM [3] mg/kg	NYSDEC Sediment Screening Value [4] mg/kg
Aluminum	7429-90-5	50	--	19300	
Antimony	7440-36-0	6	2.5	5.9	2.0
Arsenic	7440-38-2	3	0.5	8.2	6.0
Barium	7440-39-3	5	2.5	300	
Beryllium	7440-41-7	0.5	0.5	1.1	
Cadmium	7440-43-9	1	0.5	2.3	0.6
Calcium	7440-70-2	200	--	121000	
Chromium	7440-47-3	1.5	2.5	29.6	26.0
Cobalt	7440-48-4	2	0.5	30	
Copper	7440-50-8	5	2.5	33	16.0
Iron	7439-89-6	50	--	36500	20000
Lead	7439-92-1	5	0.5	24.8	31.0
Magnesium	7439-95-4	100	--	21500	
Manganese	7439-96-5	10	2.5	1060	460.0
Mercury	7439-97-6	0.2	--	0.1	0.15
Nickel	7440-02-0	4	2.5	49	16.0
Potassium	7440-09-7	200	--	2380	
Selenium	7782-49-2	4	2.5	2	
Silver	7440-22-4	1.5	0.5	0.75	1.0
Sodium	7440-23-5	300	--	172	
Thallium	7440-28-0	5	0.5	0.7	
Vanadium	7440-62-2	2.5	2.5	150	
Zinc	7440-66-6	7.5	5	110	120.0
Cyanide	7440-67-7	1	--	0.35	

Notes:

1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project. The CRQLs for soil are based on 100% solids. Samples with less than 100% solids may have CRQLs greater than those listed in the table above.
2. From CLP SOW for ILM06.x.
3. From NYSDEC TAGM #4046.
4. From NYSDEC (1999) Technical Guidance for Screening Contaminated Sediments. Benthic aquatic life chronic toxicity for freshwater sediment was used and sediment was assumed to contain 1% organic carbon.

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Table 6-M
Target Analyte List and Limits for RCRA TCLP Test

Analyte	CAS #	CRQL (µg/L) [1]	Regulatory Level (µg/L) [2]
TCLP Metals			
Arsenic	7440-38-2	1000	5000
Barium	7440-39-3	10000	100000
Cadmium	7440-43-9	100	1000
Chromium (total)	7440-47-3	1000	5000
Lead	7439-92-1	1000	5000
Mercury	7439-97-6	50	200
Selenium	7782-49-2	100	1000
Silver	7440-22-4	1000	5000
TCLP Volatiles			
Benzene	71-43-2	10	500
2-Butanone (Methylethylketone)	78-93-3	10	200000
Carbon tetrachloride	56-23-5	10	500
Chlorobenzene	108-90-7	10	100000
Chloroform	67-66-3	10	6000
1,2-Dichloroethane	107-06-2	10	500
1,1-Dichloroethylene	75-35-4	10	700
Tetrachloroethylene	127-18-4	10	700
Trichloroethylene	79-01-6	10	500
Vinyl chloride	75-01-4	10	200
TCLP Semivolatiles			
1,4-Dichlorobenzene	106-46-7	10	7500
2,4-Dinitrotoluene	121-14-2	10	130
Hexachlorobenzene	118-74-1	10	130
Hexachlorobutadiene	87-68-3	10	500
Hexachloroethane	67-72-1	100	3000
2-Methylphenol (o-Cresol)	95-48-7	10	200000
3-Methylphenol (m-Cresol)	108-39-4	10	200000
4-Methylphenol (p-Cresol)	106-44-5	10	200000
Nitrobenzene	98-95-3	10	2000
Pentachlorophenol	87-86-5	5	100000
Pyridine	110-86-1	100	5000
2,4,5-Trichlorophenol	95-95-4	10	400000
2,4,6-Trichlorophenol	88-06-2	10	2000
TCLP Pesticides			
Gamma-BHC (Lindane)	58-89-9	10	400
Chlordane	57-74-9	10	30
Endrin	72-20-8	0.5	20
Heptachlor	76-44-8	0.5	8
Heptachlor Epoxide	1024-57-3	0.5	8
Methoxychlor	72-43-5	100	10000
Toxaphene	8001-35-2	10	500
TCLP Herbicides			
2,4-Dichlorophenoxyacetic acid (2,4-D)	94-75-7	100	10000
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP; Silvex)	93-76-5	10	1000
Reactivity (HCN)		100,000	100,000
Reactivity (H_2S)		100,000	100,000

Notes:

1. Based on NYSDEC ASP Requirement for RCRA TCLP Program.
2. Based on 40CFR261.23 and 40CFR261.24.

Table 6-N

Project ARAR/TBC Limits[1] for Other Analytes

Analyte	CAS #	Groundwater ARAR/TBC [2] (µg/L)	Surface Water ARAR/TBC [3] (µg/L)	NYSDEC TAGM [4] (ug/kg)	NYSDEC Sediment Screening Value [5] (ug/kg)	Project Required RL for Aqueous[6] (ug/L)	Project Required RL for Soil/Sediment [6] (ug/kg)
Alkalinity			20000			2000	
Ammonia		2000 [7]	Note 8				
Chloride		250000	230000			1000	
Dissolved oxygen			4000 [9]			400	
Chemical Oxygen Demand						50000	
Total Kjeldahl Nitrogen (TKN)							
Hexavalent chromium		50	11			1	
Methane	74-82-8					1 [10]	
Ethane	74-84-0					2 [10]	
Ethene	74-85-1					3 [10]	
Nitrate (as N)		10000 [11]				100	
Nitrite (as N)		1000				100	
pH		6.5 – 8.5 [11] (unitless)	6.5 – 8.5 [11] (unitless)			0.1 (unitless)	
Perchlorate		6 [12]				0.6	
Phosphorus							5
Sulfatec		250000				2000	
TOC						1000	500
Total Dissolved Solids		500000					
Total nitrogen TKN							2
Total sulfides		50 [13]	2.0			0.2	
Reactivity (HCN)							250,000 [14]
Reactivity (H_2S)							500,000 [14]

Notes:

1. Project specific ARARs and TBCs may vary. This table lists commonly identified ARARs and TBCs for the Seneca project.
2. MCL, Secondary Drinking Water Regulations, or NYSDEC TOGS 1.1.1 for Class GA water, whichever is lower.
3. NYSDEC TOGS 1.1.1 for Class C water, or AWQC (USEPA, 2004) Criterion Continuous Concentration, whichever is lower. NYSDEC standards/guidelines for fresh water fish survival/propagation and wildlife protection were used; when not available, other standards/guidelines (human consumption of fish and aesthetic) were used.
4. From NYSDEC TAGM #4046.
5. From NYSDEC (1999) Technical Guidance for Screening Contaminated Sediments. Benthic aquatic life chronic toxicity for freshwater sediment was used and sediment was assumed to contain 1% organic carbon.
6. Reporting limit (RL) requirement for specific project may vary. See SS WP for project specific requirement.
7. Applies to NH3 + NH4 as N.
8. pH and temperature dependent. See NYSDEC TOGS 1.1.1 for details.
9. From NYSDEC Surface Water and Groundwater Quality Standards and Groundwater Effluent Limitations, 6 NYCRR Part 703.
10. Method quantitation limit.
11. Applies to the sum of nitrate and nitrite (expressed as N).
12. California Department of Health Services notification level.
13. Expressed as hydrogen sulfide.
14. USACE. 2002. Waste Management System; Testing and Monitoring Activities; Proposed Rule; Methods Innovation Rule

Table 7-A
Quality Control Requirements for Organic Analysis by Gas Chromatography and High-Performance Liquid Chromatography
(Methods 7580, 8081A, 8082A, and 8330)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method	QC acceptance criteria published by DoD, if available; otherwise method-specified criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria	Not applicable (NA)	This is a demonstration of ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample (e.g., LCS or PT sample). No analysis shall be allowed by analyst until successful demonstration of capability is complete.
Method detection limit (MDL) study	At initial set-up and subsequently once per 12 month period; otherwise quarterly MDL verification checks shall be performed	See 40 CFR 136B. MDL verification checks must produce a response at least 3 times greater than instrument's noise level.	Run MDL verification check at higher level and higher MDL set or reconduct MDL study	NA	Samples cannot be analyzed without a valid MDL.
Retention time window width calculated for each analyte and surrogate	At method set-up and after major maintenance (e.g., column change)	Width is ± 3 times standard deviation for each analyte retention time from 72-hour study.	NA	NA	

Table 7-A
Quality Control Requirements for Organic Analysis by Gas Chromatography and High-Performance Liquid Chromatography
(Methods 7580, 8081A, 8082A, and 8330)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Breakdown check (Endrin/ DDT Method 8081A only)	Daily prior to analysis of samples	Degradation < 20% for either endrin or DDT; Degradation <30% for sum of endrin and DDT.	Correct problem, then repeat breakdown check.	If DDT breakdown>20%:	No samples shall be run until degradation for individual compound DDT and endrin < 20% and degradation for combined DDT and endrin <30%.
Minimum three-point initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis. For HPLC, a five point initial calibration is required.	1) All single component analytes **except** alpha and delta BHC must have %RSD no greater than 20%. 2) Alpha and delta BHC must have %RSD no greater than 25%. 3) Surrogates must have %RSD no greater than 30%. 4) SOW allows up to **2** of single analytes except surrogates to fail contractual %RSD limit. **The failing analytes must have a %RSD < 30%.**	Correct problem, then repeat initial calibration.	If technical criteria were not met, qualify all associated positive results generated during the entire analytical sequence "J" and all non-detects "UJ". When %RSD > 90%, flag all non-detect results for that analyte "R" (unusable), and positive results as “J” estimated**.**	Problem must be corrected. No samples may be run until ICAL has passed. For PCB analysis, a mixture of Aroclors 1016 and 1260 is normally used to establish detector calibration linearity, unless otherwise specified by the SS-WP. In addition, a mid-level or lower standard for each of the remaining Aroclors is analyzed for pattern recognition and response factor.

Table 7-A
Quality Control Requirements for Organic Analysis by Gas Chromatography and High-Performance Liquid Chromatography
(Methods 7580, 8081A, 8082A, and 8330)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Second source calibration verification	Once after each initial calibration	Value of second source for all analytes within ± 25% of expected value (initial source)	Correct problem and verify second source standard. If that fails then repeat initial calibration.	If the %D is outside the ±25.0% range for any compound(s), qualify associated positive results for that compound "J" and non-detects "UJ". The "associated samples" are those which followed the last in-control standard up to the next passing standard containing the analyte(s) in question. If the %D is > 90%, flag all nondetects for that analyte "R" (unusable).	Problem must be corrected. No samples may be run until calibration has been verified.
Retention time window position establishment for each analyte and surrogate	Once per ICAL	The center of the retention time window shall be set at midpoint of initial calibration curve.	NA	NA	
Retention time window verification for each analyte and surrogate	Each calibration verification standard	All analytes and surrogates within established windows	Correct problem, then reprocess all samples analyzed since the last acceptable retention time check. Or, perform a new ICAL and reset retention time windows.	Flagging criteria is not appropriate for initial verification. For CCV, apply a Q-flag to all results for analytes outside the established window.	No samples shall be run without correctly set retention time windows.

Table 7-A
Quality Control Requirements for Organic Analysis by Gas Chromatography and High-Performance Liquid Chromatography
(Methods 7580, 8081A, 8082A, and 8330)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Calibration verification (initial [ICV] and continuing [CCV])	An instrument blank and the PEM must bracket one end of a 12-hour period during which sample data are collected, and a second instrument blank and the midpoint concentration of Individual Standard Mixtures A and B must bracket the other end of the 12-hour period.	All analytes within ± 25% of expected value (%D).	Correct problem, rerun calibration verification and reanalyze all samples since last successful calibration verification.	If the %D is outside the ±25.0% range for any compound(s), qualify associated positive results for that compound "J" and non-detects "UJ". The "associated samples" are those which followed the last in-control standard up to the next passing standard containing the analyte(s) in question. If the %D is > 90%, flag all nondetects for that analyte "R" (unusable).	If an individual analyte is > 25%, no samples may be analyzed until the problem has been corrected.
Method blank	A method blank must be extracted each time 20 or less field samples (excluding MS/MSD and PE samples) are extracted. A method blank shall be analyzed on each GC/EC system	No analytes detected ≥ CRQL and surrogate recoveries within 30%~150%.	Correct problem, if required, reprep then reanalyze method blank and all samples processed with the contaminated blank.	Flag sample result with a U if sample > CRQL but < or =5 x blank level; Report CRQL and qualify U if sample<CRQL and < or = 5 x blank level; no action if sample >CRQL and > 5 x CRQL.	

Table 7-A
Quality Control Requirements for Organic Analysis by Gas Chromatography and High-Performance Liquid Chromatography
(Methods 7580, 8081A, 8082A, and 8330)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Instrument blank	First analysis in a 12-hr analysis sequence	No analytes detected ≥ CRQL and surrogate recoveries within 30%~150%.	Correct problem, reanalyze instrument blank and associated samples.		
Laboratory control sample (LCS) containing all analytes required to be reported by the project or contract	One LCS for every group of samples in the Sample Delivery Group.	QC acceptance criteria specified in CLP and those specified in Table 9.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated batch for failed analytes in all samples in the associated preparatory batch, if sufficient sample material is available	If corrective action fails, or sufficient sample volume is not available for reprep, apply professional judgment to determine necessary quailifier for specific analyte(s) in all samples in the associated preparatory batch.	LCS acceptance criteria MUST be met before data are reported. LCS contamination or any LCS analyzed not meeting the criteria will require re-extraction and re-analysis at no additional cost.
Matrix spike (MS)	A matrix spike must be performed for the following, whichever is most frequent: 1) Each SDG, 2) Each group of 20 field samples. 3) Each group of field samples of a similar concentration level.	For matrix evaluation, use QC acceptance criteria specified by CLP and those specified in Table 9.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	No action is taken based upon MS/MSD data alone. MS/MSD results may be used in conjunction with other QC criteria to determine the need for data qualification. The validator using **professional judgment** has several options: 1) Do nothing; 2) Qualify only the affected analyte in the unspiked sample; 3) Qualify all analytes in the unspiked sample; 4) Qualify only the affected analyte in all samples. This must be supported by details; 5) Qualify only the affected analyte or all of the analytes if recovery is < 10%	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.

Table 7-A
Quality Control Requirements for Organic Analysis by Gas Chromatography and High-Performance Liquid Chromatography
(Methods 7580, 8081A, 8082A, and 8330)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Matrix spike duplicate (MSD) or sample duplicate	A matrix spike duplicate or sample duplicate must be performed for the following, whichever is most frequent: 1) Each SDG, 2) Each group of 20 field samples, 3) Each group of field samples of a similar concentration level. For 8330, one laboratory duplicate should be submitted for each extraction batch.	RPD (between MS and MSD or sample and sample duplicate) meets criteria specified in Table 9.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	Professional judgment, see above.	The data shall be evaluated to determine the source of difference.

Table 7-A
Quality Control Requirements for Organic Analysis by Gas Chromatography and High-Performance Liquid Chromatography
(Methods 7580, 8081A, 8082A, and 8330)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Surrogate spike (analytes identified in Table 8)	All field and QC samples	QC acceptance criteria for surrogate specified in Table 8	For QC and field samples, reanalyze sample. If surrogate recovery is still out, identify the cause of the problem. If possible, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	Qualify data in accordance with Region 2 SOP. In brief, 1) If surrogate on both columns is below limit but >10%, check chromatograms for interference and qualify affected analytes 2) If surrogate on both columns is below limit but > 10%, J non-detects and positive hits. 3) If recoveries for both surrogates on both columns are below limit but >10%, J positive results and UJ non-detects. 4) If recoveries are above limit for both surrogates on both columns, J positive values. 5) If both surrogates on one column are below limit but > 10%, use the data from the other column, providing both surrogates on that column are within limits. 6) If recovery is <10% for either surrogate on any column, and no chromatographic or matrix interference is visible, J positive results and R non-detects.	Alternative surrogates are recommended when there is obvious chromatographic interference.

Table 7-A
Quality Control Requirements for Organic Analysis by Gas Chromatography and High-Performance Liquid Chromatography
(Methods 7580, 8081A, 8082A, and 8330)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Confirmation of positive results (second column or second detector)	All analytes detected above the MDL require confirmation on a second column or second detector.	Results between two columns %D ≤ 25%. (when higher value is compared to lower value)	NA	Qualify data in accordance with Region 2 SOP. In brief, %D=0 - 25%, no action %D=26 - 70%, "J" %D=71 - 100%, "JN" %D=100-200% (No Interference) "R" %D=100 - 200% (Interference detected), "JN" %D> 50% (Pesticide value is < CRQL), "U" %D> 200% "R"	Report the lower of two results unless QA/QC issues with the column.
Results reported between MDL and RL	NA	NA	NA	Apply J to all results below CRQL. Hits well below the CRQLs (less than 1/2 the CRQL value) may be column/background noise and using discretion may not be reported.	

Note:
QA/QC requirements are based on the CLP OLM04.3 SOP. If SW 846 methods or other equivalent methods are chosen for specific project, QA/QC requirements should be consistent with the specifications provided by the method or the SS-WP. Data validation should be conducted in accordance with the Region 2 SOPs for the specific method.

Table 7-B
Quality Control Requirements for Organic Analysis by Gas Chromatography/Mass Spectroscopy (Methods 8260B, 8270C, 524.2) and GC/FID (Method 8015B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method	QC acceptance criteria published by DoD, if available; otherwise method-specific criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria	NA	A demonstration of ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample (e.g., LCS or PT). No analysis shall be allowed until demonstration of capability is complete.
MDL study	At initial set-up and subsequently once per 12-month period; otherwise quarterly MDL verification checks shall be performed	See 40 CFR 136B. MDL verification checks must produce a response at least 3 times greater than instrument's noise level.	Run MDL verification check at higher level and higher MDL set or reconduct MDL study	NA	Samples cannot be analyzed without a valid MDL.
Tuning (MS methods only)	Prior to calibration and every 12 hours during analysis	Refer to Table 1 in Exhibit D of CLP OLC03.2 (December 2000) and OLM04.3 (March 2003) for specific requirements.	Retune instrument and verify. Rerun affected samples.	Flagging criteria is not appropriate	Problem must be corrected. No samples may be accepted without a valid tune.

Table 7-B
Quality Control Requirements for Organic Analysis by Gas Chromatography/Mass Spectroscopy (Methods 8260B, 8270C, 524.2) and GC/FID (Method 8015B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Minimum five-point initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis, whenever corrective action is taken which may affect initial calibration, and whenever calibration acceptance criteria are not met.	Refer to CLP OLC03.2 (December 2000) and OLM04.3 (March 2003) for specific requirements. VOC: Table 5 in Exhibit D, OLM04.3; Table D-2 in Exhibit D, OLC03.2 SVOC: Table 5 in Exhibit D, OLM04.3; Table D-4 in Exhibit D, OLC03.2 Up to two compounds may fail the criteria and still meet the minimum RRF and %RSD requirements. However, these compounds must have a minimum RRF greater than or equal to 0.010, and the %RSD must be less than or equal to 40.0 percent.	Correct problem then repeat initial calibration.	Qualify in accordance with Region 2 SOP. If %RSD is > 30.0%, J associated detects. When %RSD is>90%, R non-detects and J detects**.** If the average RRF is < 0.05, qualify associated non-detects with an "R" and flag associated positive data as estimated "J".	Problem must be corrected. No samples may be run until ICAL has passed.
Retention time window position establishment for each analyte and surrogate	Once per ICAL	Position shall be set using the midpoint standard of the initial calibration curve.	NA	NA	
Evaluation of relative retention times (RRT)	Each calibration verification standard	All analytes and surrogates within established windows	Correct problem, then reprocess all samples analyzed since the last acceptable retention time check. Or, perform a new ICAL and reset retention time windows.	Professional judgment. If incorrect identifications were made, data should be rejected, flagged N or changed to not detected at reporting limit.	

Table 7-B
Quality Control Requirements for Organic Analysis by Gas Chromatography/Mass Spectroscopy (Methods 8260B, 8270C, 524.2) and GC/FID (Method 8015B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Calibration verification (CV)	Daily, before sample analysis, after injection of instrument performance compound and every 12 hours of analysis time	Refer to CLP OLC03.2 (December 2000) and OLM04.3 (March 2003). VOC: Table 5 in Exhibit D, OLM04.3; Table D-2 in Exhibit D, OLC03.2 SVOC: Table 5 in Exhibit D, OLM04.3; Table D-4 in Exhibit D, OLC03.2 Up to two compounds may fail the criteria and still meet the minimum RRF and %RSD requirements. These compounds must have a minimum RRF no less than 0.010, and %RSD must be less than or equal to 40.0 percent.	Correct problem, rerun CV. If that fails, then repeat initial calibration and reanalyze all affected samples.	J both detects and non-detects for the outlier compound(s) if %D>25%. When %D is > 90%, R non-detects and J detects**.** If any RRF is < 0.05, R associated non-detects and J associated detects.	
Internal standards	With every continuing calibration, and with every project sample	Internal standard areas of every sample and blank should be within the upper and lower limits (-50% to +100%) for each continuing calibration; the retention times of the internal standards should be within 30 seconds of the associated calibration standard.	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory. See corrective action for CV.	See Region 2 SOPs. If IS area count is outside limit, J associated results. Do not qualify nondetects when associated IS area counts are > 100%. If area counts are < 25% of 12-hr IS area, or if performance exhibits a major abrupt dropoff, R associated nondetects and J detects.	Sample results are not acceptable without a valid CV-IS.

Table 7-B
Quality Control Requirements for Organic Analysis by Gas Chromatography/Mass Spectroscopy (Methods 8260B, 8270C, 524.2) and GC/FID (Method 8015B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Method blank	SVOC: One per preparatory batch (or 20 field samples, whichever is more frequent), VOC: analyzed every 12-hr time period on each GC/MS system, before any samples, and for each matrix.	The concentration of each target compound found in the storage and method blanks must be less than its CRQL, except for methylene chloride and cyclohexane which must be less than 10 times their respective CRQLs, acetone and 2-butanone, which must be less than two times their respective CRQLs, and phthalate esters, which must be less than 5 times CRQLs.	Correct problem. All samples processed within the 12-hour time period with a method blank or instrument blank that does not meet the blank technical acceptance criteria will require reanalysis at no additional cost.	For common analytes, flag sample result with a U if sample >CRQL but ≤10xblank level; Report CRQL and qualify U if sample<CRQL and ≤10xblank level; no action if sample >CRQL and >10xCRQL. For other analytes, flag sample result with a U if sample > CRQL but ≤5xblank level; Report CRQL and qualify U if sample<CRQL and ≤5xblank level; no action if sample >CRQL and >5xCRQL.	The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds.
LCS containing all analytes required to be reported by the project or CLP	One LCS per preparatory batch	QC acceptance criteria specified by the laboratory or 70~130% when laboratory advisory limits are not available.	Correct problem, then reprep and reanalyze the LCS and all associated samples for failed analytes, if sufficient sample material is available.	When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.	When MS results indicate a potential problem due to sample matrix, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

Table 7-B
Quality Control Requirements for Organic Analysis by Gas Chromatography/Mass Spectroscopy (Methods 8260B, 8270C, 524.2) and GC/FID (Method 8015B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
MS	A matrix spike must be performed for the following, whichever is most frequent: 1) Each SDG, 2) Each group of 20 field samples, 3) Each group of field samples of a similar concentration level.	For matrix evaluation, use QC acceptance criteria specified by CLP and those specified in Table 9.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	No action is taken based upon MS/MSD data alone. MS/MSD results may be used in conjunction with other QC criteria to qualify data. The validator using **professional judgment** has several options: 1) Do nothing 2) Qualify only the affected analyte in the unspiked sample 3) Qualify all of the analytes in the unspiked sample 4) Qualify only the affected analyte in all samples. This must have supporting details to document this action 5) Qualify only the affected analyte or all of the analytes if recovery is < 10%	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.

Table 7-B
Quality Control Requirements for Organic Analysis by Gas Chromatography/Mass Spectroscopy (Methods 8260B, 8270C, 524.2) and GC/FID (Method 8015B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
MSD or sample duplicate	A matrix spike duplicate or sample duplicate must be performed for the following, whichever is most frequent: 1) Each SDG, 2) Each group of 20 field samples, 3) Each group of field samples of a similar concentration level.	RPD (between MS and MSD or sample and sample duplicate) meets criteria specified in Table 9.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	Professional judgment, see above.	The data shall be evaluated to determine the source of difference.

Table 7-B
Quality Control Requirements for Organic Analysis by Gas Chromatography/Mass Spectroscopy (Methods 8260B, 8270C, 524.2) and GC/FID (Method 8015B)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Surrogate spike (analytes identified in Table 8)	All field and QC samples	QC acceptance criteria for in Table 8.	For VOC, if any surrogate recovery fails, correct problem, then all samples with failing surrogates must be reanalyzed. For SVOC, if two or more surrogate within the same fraction fail, correct problem, then all samples with failing surrogates in the associated preparatory batch must be reprepped and /or reanalyzed.	For VOC, if recoveries ≥10% but outside limits, J all detects; UJ non-detects where recovery is less than lower limit. For SVOC, if two BN or acid surrogate recoveries exceed limits but ≥10%, for the affected fraction only, qualify positive results as J and flag all non-detects as UJ when recoveries are less than lower limit. For VOC and SVOC, If any surrogate recovery < 10%, qualify associated positive results as J and non-detects as R.	
Results reported between MDL and RL	NA	NA	NA	Apply J to all results between MDL and RL.	

Note:
QA/QC requirements are based on the CLP OLM04.3 SOP. If SW 846 methods or other equivalent methods are chosen for specific project, QA/QC requirements should be consistent with the specifications provided by the method or the SS-WP. Data validation should be conducted in accordance with the Region 2 SOPs for the specific method.

Table 7-C
Quality Control Requirements for Inorganic Analysis by Inductively Coupled Plasma (ICP) and Atomic Absorption Spectroscopy (AA) (Methods 6010B And 7000A Series)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method	QC acceptance criteria published by DoD, if available; otherwise method-specified criteria	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria	NA	This is a demonstration of analyst ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample (e.g., LCS or PT sample). No analysis shall be allowed by analyst until successful demonstration of capability is complete.
MDL study	At initial set-up and subsequently once per 12 months; otherwise quarterly MDL verification checks shall be performed	See 40 CFR 136B. MDL verification checks must produce a response at least 3 times greater than instrument noise level.	Run MDL verification check at higher level and higher MDL set or reconduct MDL study	NA	Samples cannot be analyzed without a valid MDL.
Instrument detection limit (IDL) study (ICP only)	Every 3 months	Detection limits established shall be ≤ CRDL.	NA	NA	Samples cannot be analyzed without a valid IDL.
Linear range or high-level calibration check standard (ICP only)	The upper limit of the linear range should be established prior to the start of contract analyses and at least quarterly thereafter.	NA	NA	NA	No samples may be analyzed without a valid upper limit of linear range established.

Table 7-C
Quality Control Requirements for Inorganic Analysis by Inductively Coupled Plasma (ICP) and Atomic Absorption Spectroscopy (AA) (Methods 6010B And 7000A Series)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Initial calibration for all analytes (ICAL)	Daily initial calibration prior to sample analysis (ICP: minimum one high standard and a blank; GFAA: minimum three standards and a blank; CVAA: minimum 4 standards and a blank)	ICP: No acceptance criteria unless more than one standard is used, in which case $r \geq 0.995$. GFAA: $r \geq 0.995$ CVAA: $r \geq 0.995$	Correct problem and repeat initial calibration.	Flag as J all associated results.	Problem must be corrected. No samples may be run until ICAL has passed.
Second source calibration verification	Once after each initial calibration, prior to sample analysis	All analyte(s) within ± 10% of expected value.	Correct problem and verify second source standard. If that fails, then repeat initial calibration.	J all detects with %R between 75-89% (65-79% for Hg; 70-84% for CN) or 111-125% (121-135% for Hg; 116-130% for CN) recovery. Qualify results <IDL as UJ if ICV %R is 75-89% (CN, 70-84%; HG, 65-79%). Reject data if recovery of the ICV is outside the range 75-125% (CN, 70-130%; Hg, 65-135%). Qualify five samples on either side of verification standard out of control limits.	Problem must be corrected. No samples may be run until calibration has been verified as acceptable.
Continuing calibration verification (CCV)	After every 10 samples and at the end of the analysis sequence	All analyte(s) within ± 10% of expected value	Correct problem, rerun calibration verification. If fails, repeat initial calibration and reanalyze samples.	Save as above.	Problem must be corrected. Results may not be reported without a valid CCV.

Table 7-C
Quality Control Requirements for Inorganic Analysis by Inductively Coupled Plasma (ICP) and Atomic Absorption Spectroscopy (AA) (Methods 6010B And 7000A Series)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Low level calibration check standard (ICP only)	Daily after ICV/ICB and immediately preceding the Interference Check Sample (ICS) analyses; in addition, at the end of each sample analysis run and at a frequency of not less than once per 20 analytical samples[1] per analysis run, followed by CCV/CCB.	The percent recovery of the CRI should fall within 70-130% (50-150% for antimony, lead, and thallium)	Reanalyze CRI, if still not within the limits, correct problem, recalibrate instrument, then reanalyze.	If the recovery of the standard is between 50-69%, flag all positive sample results as "J" and all non-detect results as "UJ"; If the recovery is between 131-150%, flag positive sample results as "J"; If the recovery is less than 50%, flag all data as "R"; If the recovery is greater than 150%, flag all positive sample results as "R".	No samples may be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be less than or equal to the reporting limit. If a multipoint calibration is performed and the low point of the calibration is at or below the reporting limit, no low level calibration check is necessary.

Table 7-C
Quality Control Requirements for Inorganic Analysis by Inductively Coupled Plasma (ICP) and Atomic Absorption Spectroscopy (AA) (Methods 6010B And 7000A Series)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Preparation blank	One per preparatory batch, or one per SDG, whichever is more frequent.	No analytes detected ≥ CRDL. For common laboratory contaminants, no analytes detected ≥ RL.	If preparation blank>CRDL, all associated samples with concentrations less than 10 times blank and above CRQL shall be redigested and re-analyzed. If preparation blank < -CRDL, all samples reported below 10 x CRDL associated with the blank, shall be redigested and re-analyzed with appropriate new QC.	Flagging criteria is not appropriate.	
Calibration blank	Immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent.	No analytes detected ≥ CRDL or 2xIDL if IDL > CRDL.	Correct problem, then reanalyze calibration blank and all associated samples.	Flag as (J) positive sample results when raw sample value is less than or equal to calibration blank value analyzed between calibration blank with value over CRDL (or 2xIDL) and nearest good calibration blank. Flag five samples on either side of the calibration blank outside limits.	

Table 7-C
Quality Control Requirements for Inorganic Analysis by Inductively Coupled Plasma (ICP) and Atomic Absorption Spectroscopy (AA) (Methods 6010B And 7000A Series)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Interference check solutions (ICP only)	At the beginning (after ICV) and end of an analytical run, and at a frequency of not less than once per 20 analytical samples per analysis run.	Within ±20% of true value	Terminate analysis, locate and correct problem, recalibrate instrument, reanalyze ICS, reanalyze all affected samples.	If ICS recovery is between 121-150%, flag associated positive sample results "J"; if ICS recovery falls within 50-79%, flag associated positive sample results as "J" and associated non-detect sample results as "UJ"; If ICS recovery is <50%, flag all associated results as "R"; if ICS recovery is > 150%, flag all positive results as "R".	
LCS containing all analytes required to be reported by the project or contract	One LCS per preparatory batch, or per SDG, whichever is more frequent for each matrix (aqueous and solid).	Within ±20% of true value for aqueous LCS. Within the USEPA specified limits for solid LCS provided by USEPA.	If % recovery for aqueous LCS falls outside 80 - 120% (exception: Ag and Sb), or if results for the solid LCS fall outside EPA limits, analyses must be terminated, problem corrected, and previous samples associated with the LCS redigested and reanalyzed..	If aqueous LCS recovery is < 50%, R all data; J associated data if LCS recovery is between 50% and 79%; J all detects if recovery is between 121% and 150%; R all detects if recovery is greater than 150%. If solid LCS recovery is higher than limits, J all associated detects. If solid LCS recovery is lower than limits, J all associated data.	

Table 7-C
Quality Control Requirements for Inorganic Analysis by Inductively Coupled Plasma (ICP) and Atomic Absorption Spectroscopy (AA) (Methods 6010B And 7000A Series)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Serial dilution test (ICP only)	One sample from each SDG and matrix.	Five-fold dilution must agree within ± 10% of the original measurement if concentration is sufficiently high (i.e., >10IDL).		J all sample data>10xIDLs (or >CRDL when 10xIDL<CRDL) for which %D is greater than 10% but less than 100%. R associated results no less than 10xIDLs (or >CRDL when 10xIDL<CRDL) for which %D is no less than 100%.	Only applicable for samples with concentrations > 10 x IDL.
Post digestion spike (ICP and cyanide)	When MS test fails.	Recovery within 75-125% of expected results	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	No action is taken based upon PDS data alone. However, using informed professional judgment, the PDS results may be used in conjunction with other QC criteria to determine the need for qualification of the data.	
Recovery test (GFAA only)	When dilution test fails.	Recovery within 85-115% of expected results.	Run samples by method of standard addition (MSA) or see flagging criteria.	Apply J to all sample results (for same matrix) in which MSA was not run when recovery is outside of 85-115% range.	
Method of standard addition (MSA)	When matrix interference is suspected	NA	NA	NA	Document use in the case narrative.

Table 7-C
Quality Control Requirements for Inorganic Analysis by Inductively Coupled Plasma (ICP) and Atomic Absorption Spectroscopy (AA) (Methods 6010B And 7000A Series)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
MS	One MS every 20 project samples, or per SDG, whichever is more frequent per matrix.	Recovery within 75-125% of expected results	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For aqueous, if < 30%, R all associated results; if between 30-74%, J associated results, if between 126-150%, J associated detects; if >150%, R associated detects. For solid samples, if <10%, R associated data; if between 10-74%, J all associated data; if between 126-200%, J associated detects; if >200%, R associated detects.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
MSD or sample duplicate	One every 20 project samples, or per SDG, whichever is more frequent, per matrix	RPD < 20%, or difference <CRDL when both results<5CRDL(between MS and MSD or sample and sample duplicate)	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J if acceptance criteria are not met (RPD<50% for aqueous and RPD<100% for soil; difference<CRDL for aqueous and difference<2CRDL for soil when both concentrations <5CRDL).	The data shall be evaluated to determine the source of difference.
Results reported between IDL and CRDL	NA	NA	NA	Apply J to all results between IDL and CRDL.	

Note:
QA/QC requirements are based on the CLP ILM06.X SOP. If SW 846 methods or other equivalent methods are chosen for specific project, QA/QC requirements should be consistent with the specifications provided by the method or the SS-WP. Data validation should be conducted in accordance with the Region 2 SOPs for the specific method.

Table 7-D
Quality Control Requirements for Trace Metals Analysis by Inductively Coupled Plasma Mass Spectrometry (Method 6020)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel or test method	QC acceptance criteria published by DoD, if available; otherwise method-specified criteria	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria	NA	A demonstration of analyst ability to generate acceptable accuracy and precision using four replicate analyses of a QC check sample (e.g., LCS or PT). No analysis shall be allowed until demonstration of capability is complete.
MDL study	At initial set-up and once per 12 months for each digestion approach and instrument used, and after major instrument maintenance/ condition change.	See 40 CFR 136B. MDL verification checks must produce a response at least 3 times greater than instrument noise level.	Run MDL verification check at higher level and higher MDL set or reconduct MDL study.	NA	Samples cannot be analyzed without a valid MDL.
IDL study	Every 3 months	Detection limits established shall be ≤ CRDL.	NA	NA	Samples cannot be analyzed without a valid IDL.
Tuning (MS methods only)	Prior to initial calibration	Per 6020 (5.8) and CLP ILM05.3	Retune instrument then reanalyze tuning solutions.	Flagging criteria is not appropriate.	No analysis shall be performed without a valid MS tune.
Initial calibration (ICAL)	Daily prior to sample analysis, or after changes or corrections to the system. Minimum a high standard and a blank	If more than one calibration standard is used, $r \geq 0.995$	Correct problem, then repeat initial calibration.	Flag as J all associated results.	Problem must be corrected. No samples may be run until ICAL has passed.

Table 7-D
Quality Control Requirements for Trace Metals Analysis by Inductively Coupled Plasma Mass Spectrometry (Method 6020)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Second source calibration verification (ICV)	Once after each ICAL, prior to beginning a sample run	Value of second source for all analytes within ± 10% of expected value (initial source)	Correct problem and verify second source standard. If that fails, then repeat initial calibration.	Flag as J all positive data (not flagged with a "U") analyzed between a calibration verification with %R between 75-89% or 111-125% recovery and nearest good calibration standard. Qualify results <IDL as estimated (UJ) if the ICV is 75-89%. Reject data if recovery of the ICV is outside the range 75-125%. Qualify five samples on either side of verification standard out of control limits.	Problem must be corrected. No samples may be run until calibration has been verified.
Continuing calibration verification (CCV)	After every 10 samples and at the end of the analysis sequence	All analytes within ± 10% of expected value	Correct problem, rerun calibration verification. If that fails, then repeat initial calibration. Reanalyze all samples since the last successful calibration.	Flag as J all positive data (not flagged with a "U") analyzed between a calibration verification with %R between 75-89% or 111-125% recovery and nearest good calibration standard. Qualify results <IDL as estimated (UJ) if the ICV is 75-89%. Reject data if recovery of the CCV is outside the range 75-125%. Qualify five samples on either side of verification standard out of control limits.	Problem must be corrected. Results may not be reported without a valid CCV.

Table 7-D
Quality Control Requirements for Trace Metals Analysis by Inductively Coupled Plasma Mass Spectrometry (Method 6020)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Low-level calibration check standard (CRI)	Daily, after ICV/ICB and immediately preceding the Interference Check Sample (ICS) analyses. In addition, the lab shall analyze the CRI at the end of each sample analysis run and at a frequency of not less than once per 20 analytical samples[1] per analysis run. These subsequent analyses of the CRI shall be immediately followed by CCV/CCB analyses.	Within ± 30% of expected value (within ± 50% for cobalt, manganese, and zinc).	Correct problem, then reanalyze.	Flag as J all sample results within the affected range if the recovery of the standard is between 50-69%; flag only positive data within the affected range if the recovery is between 131-150%; reject all data within the affected range if the recovery is less than 50%; reject only positive data within the affected range if the recovery is greater than 150%. Qualify 50% of the samples on either side of CRI standard outside the control limits.	No samples may be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be less than or equal to the reporting limit.
Linear range or high-level calibration check standard	The upper limit of the linear range should be established prior to the start of contract analyses and at least quarterly thereafter.	NA	NA	NA	No samples may be analyzed without a valid upper limit of linear range established.

Table 7-D
Quality Control Requirements for Trace Metals Analysis by Inductively Coupled Plasma Mass Spectrometry (Method 6020)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Preparation blank	One per preparatory batch, or one per SDG, whichever is more frequent.	No analytes detected ≥ CRDL. For common laboratory contaminants, no analytes detected ≥ RL.	If preparation blank>CRDL, all associated samples with concentrations less than 10 times the blank concentration and above the CRQL shall be redigested and re-analyzed with appropriate new Quality Control (QC) for that analyte. If preparation blank < -CRDL, all samples reported below 10 x CRDL associated with the blank, shall be redigested and re-analyzed with appropriate new QC.	Flagging criteria is not appropriate.	No samples may be analyzed without an acceptable method blank.
Calibration blank	Immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent.	No analytes detected ≥ CRDL or 2IDL if IDL > CRDL.	Correct problem, then reprep and reanalyze calibration blank and previous 10 samples.	Flag as (J) positive sample results when raw sample value is less than or equal to calibration blank value analyzed between calibration blank with value over CRDL (or 2xIDL) and nearest good calibration blank. Flag five samples on either side of the calibration blank outside limits.	
Interference check solutions	The interference check solutions shall be	Within ±20% of true value, or ±3 times	Terminate analysis, locate and correct	If recovery is between 121-150%, flag all positive results	

Table 7-D
Quality Control Requirements for Trace Metals Analysis by Inductively Coupled Plasma Mass Spectrometry (Method 6020)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
(ICS-A and ICS-AB)	analyzed at the beginning (after ICV) and end of an analytical run or twice during an 8-hour working shift, whichever is more frequent.	the CRQL, whichever is greater.	problem, recalibrate instrument, reanalyze ICS, reanalyze all affected samples.	"J"; If recovery falls within 50-79%, flag all results as "J"; If recovery is <50%, flag all results "R"; if ICS recovery is > 150%, flag all positive results as "R".	
LCS containing all analytes required to be reported by the project or contract	One LCS per preparatory batch, or per SDG, whichever is more frequent for each matrix (aqueous and solid)..	Within ±20% of true value for aqueous LCS. Within the USEPA specified limits for solid LCS provided by USEPA.	If % recovery for aqueous LCS falls outside 80 - 120% (exception: Ag and Sb), or if results for solid LCS fall outside EPA limits, analyses must be terminated, problem corrected, and previous samples associated with the LCS redigested and reanalyzed..	If aqueous LCS recovery is < 50%, R all data; if LCS recovery is between 50% and 79% J associated data; if recovery is between 121% and 150% J detects; if recovery is greater than 150% R all detects. If solid LCS recovery is higher than limits, qualify all associated positive data as J. If solid LCS recovery is lower than limits, J associated data.	
Serial dilution test	One sample from each SDG and matrix.	Five-fold dilution must agree within ± 10% of the original measurement if concentration is sufficiently high (i.e., >10IDL).		J associated sample data >10xIDLs (or >CRDL when 10xIDL<CRDL) for which percent difference is greater than 10% but less than 100%. R associated results no less than 10xIDLs (or >CRDL when 10xIDL<CRDL) for which %D is no less than 100%.	Only applicable for samples with concentrations > 10 x IDL.
Post digestion spike	When MS test fails.	Recovery within 75-125% of expected results	Examine project DQOs. Contact client for additional measures.	NA.	

Table 7-D
Quality Control Requirements for Trace Metals Analysis by Inductively Coupled Plasma Mass Spectrometry (Method 6020)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
MS	One MS every 20 project samples, or per SDG, whichever is more frequent per matrix.	Recovery within 75-125% of expected results	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For aqueous, if < 30%, reject all associated aqueous data; if between 30-74%, flag all associated aqueous data as "J"; if between 126-150%, flag all positive sample results as "J"; if >150%, reject all positive sample results. For solid samples, if <10%, reject all associated data; if between 10-74%, flag all associated data as "J"; if between 126-200%, flag as "J" all positive sample results; if >200%, reject all positive sample results.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
MSD or sample duplicate	One every 20 project samples, or per SDG, whichever is more frequent, per matrix	RPD < 20%, or difference <CRDL when both results<5CRDL(between MS and MSD or sample and sample duplicate)	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J if acceptance criteria are not met (RPD<50% for aqueous and RPD<100% for soil; difference<CRDL for aqueous and difference<2CRDL for soil when both concentrations <5CRDL).	The data shall be evaluated to determine the source of difference.

Table 7-D
Quality Control Requirements for Trace Metals Analysis by Inductively Coupled Plasma Mass Spectrometry (Method 6020)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Data Validation Flagging Criteria	Comments
Internal standards (IS)	Every sample	IS intensity within 60-125% of intensity of the IS in the calibration blank	Original samples should be diluted by a factor of two, internal standards added, and the sample re-analyzed. Report the results of reanalysis if the internal standard responses are within the limits. If internal standard responses are still not within limits, note in SDG Narrative and report the results of the undiluted original sample analysis.	Flagging criteria is not appropriate.	No samples should be reported without passing internal standards.
Results reported between IDL and CRDL	NA	NA	NA	Apply J to all results between IDL and CRDL.	

Note:
QA/QC requirements are based on the CLP ILM06.X SOP. If SW 846 methods or other equivalent methods are chosen for specific project, QA/QC requirements should be consistent with the specifications provided by the method or the SS-WP. Data validation should be conducted in accordance with the Region 2 SOPs for the specific method.

Table 7-E
Quality Control Requirements for Perchlorate by Ion Chromatography (Method 314.0)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Initial Demonstration of Capability (IDC)	Prior to beginning any analysis batch.	See Table 5 of Method 314.0.	NA	
Matrix Conductivity Threshold (MCT)	As part of the initial demonstration of capability. See section 9.2.8 of Method 314.0.	MCT, based on linear regression, is the matrix conductance for which the peak area-to-height ratio percent difference exceeds 20%. See Table 5 of Method 314.0.	NA	
Method Detection Limit (MDL)	An MDL study is conducted at initial setup and subsequently once per 12-month period and when major changes occur in the methods operating procedures. If no changes have been made, quarterly MDL verification may be performed in lieu of yearly MDL study.	MDL study must be performed in the matrix of interest using a standard at a concentration that is 1 to 10 times the estimated MDL value. MDL must be validated through the analysis of a low-level spike at ~ 2 times MDL taken through the entire preparation process. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or perform the MDL study again.	Samples cannot be analyzed without a valid MDL.
Limit of Quantitation (LOQ; called MRL, Method Reporting Level in 314.1)	With every initial calibration.	Documented in the specific matrix of concern, at or below the applicable regulatory limit. Equal to lowest calibration standard. At least 3 times the MDL/LOD. The LOQ must be verified in a solution prepared at the MCT.	Flag all results between LOD and LOQ as "J".	
Retention-Time	At method setup and after major maintenance (e.g., column change).	Width is + 3 times standard deviation for each analyte retention time from 72-hour study.	NA	

Table 7-E
Quality Control Requirements for Perchlorate by Ion Chromatography (Method 314.0)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Holding time (HT)	Applies to all samples.	HT < 28 days (to be consistent with other EPA requirements).	All data analyzed outside the required holding time should be qualified using professional judgment. If holding time is only slightly exceeded, data may be qualified with "J" or not at all. If holding time is grossly exceeded, data should be rejected (flagged as "R").	
Initial Calibration (ICAL)	Initial calibration prior to sample analysis.	Minimum of 5 calibration standards to establish linearity (daily), r2 > 0.995.	Correct problem, then repeat initial calibration. Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.
Second Source Calibration Verification (SSCV)	Once after each multipoint calibration.	Value of second source for perchlorate within + 10% of expected value (initial source).	Correct problem and verify second source standard. Rerun SSCV. If that fails, correct problem and repeat initial calibration.	Problem must be corrected. No samples may be run until SSCV has passed.
Initial Calibration Verification Standard (ICV)	After initial calibration, with each analysis batch, analysis of a standard at the LOQ	Recovery must be 85-115% of true value. Note: Method 314.0 requires + 25%; however, the DoD-QSM requires the acceptance criteria for the ICV to be the same as the continuing calibration verifications. As the QSM requirements are more stringent, they supersede the method requirements.	Correct problem and rerun ICV. If that fails, correct problem and repeat initial calibration. Flagging criteria are not appropriate. No samples may be run until calibration has been verified.	Problem must be corrected. No samples may be run until calibration has been verified.

Table 7-E
Quality Control Requirements for Perchlorate by Ion Chromatography (Method 314.0)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Instrument Performance Check (IPC)	One per analytical batch .Analysis of a standard containing mid-level perchlorate and interfering anions bracket each analytical batch to verify method performance at the matrix conductivity threshold. At least one IPC must be analyzed daily.	IPC conductance within + 10% of original measured value. Peak area-to-height ratio percent difference < 20% (compared to peak area-to-height ratio of the LCS). Perchlorate quantitated between 80 and 120% of fortified level. < 5% shift in perchlorate retention time.	Correct problem and then reanalyze all samples in that batch. If poor recovery from the cleanup filters is suspected, a different lot of filters must be used to re-extract all samples in the batch. If column degradation is suspected, a new column must be calibrated before the samples can be reanalyzed.	No samples may be reported as associated with a failing IPC.
Continuing Calibration Verification Standard (CCV)	Alternate analysis of mid-level standard and a standard at the LOQ after every 10 samples. At the end of the batch, both standards should be analyzed. All samples should be bracketed by the analysis of a standard demonstrating that the system was capable of accurately detecting and quantifying perchlorate.	Recoveries must fall between 85 and 115%.	Correct problem and rerun CCV and all samples analyzed since last successful CCV. If that fails, apply Q-flag to all results in all samples since the last acceptable calibration verification, if reanalysis is not possible.	No samples may be analyzed until the problem has been corrected.
Method Blank or Pretreated Laboratory Reagent Blank	One per batch (up to 20 samples). Must undergo same pretreatment process that was performed on the samples.	<½ of the RL	Correct problem, re-prep, then reanalyze method blank and all samples processed with the contaminated blank. Apply B-flag to all results for the specific analytes in all samples in the associated preparatory batch if reanalysis is unsuccessful.	N/A

Table 7-E
Quality Control Requirements for Perchlorate by Ion Chromatography (Method 314.0)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Pretreated QC	REQUIRED once per analytical batch if batch includes samples that have exceeded the MCT and have been pretreated in any way to reduce the common anion levels. Pretreated method blanks, LCS, ICS, and matrix spikes should be analyzed if any samples in the batch have required pretreatment to reduce common anions.	Apply criteria as stated above for individual QC elements.	Use corrective action/flagging criteria as stated above for individual QC elements.	Pretreated samples must have associated pretreated QC samples.
Laboratory Control Sample (LCS)	Once per analytical batch following the ICV. Calculate %Recovery prior to analyzing samples.	%Recovery within 85-115%.	Correct problem, then re-prep and reanalyze the LCS and all associated samples. If corrective action fails, all data should be rejected (flagged as "R")	Sample results from batches that fail the LCS are invalid.
Matrix Spikes (MS)	One per 20 samples per matrix.	%Recovery within 80-120%.	No action is taken based upon MS/MSD data alone. However, using informed professional judgment, the MS/MSD results may be used in conjunction with other QC criteria to determine the need for qualification of the data.	For matrix evaluation only. If MS results are outside limits, the data must be evaluated to determine the source of the difference and to determine if there is a matrix effect or analytical error.
Matrix Spike Duplicates or Laboratory Duplicates (MS and MSD)	one per 20 samples per matrix.	%Recovery within MS limits, RPD < 15%.	Flag all positive sample results as "J".	Evaluate the data to determine the source of the difference.

Table 7-F
Quality Control Requirements for Perchlorate by MS Methods (Method EPA 331.0, EPA 332.0, SW6850)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Holding Time (HT)	All samples	HT < 28 days	All data analyzed outside the required holding time should be qualified using professional judgment. If holding time is only slightly exceeded, data may be qualified with "J" or not at all. If holding time is grossly exceeded, data should be rejected (flagged as "R").	No criteria exist.
Limit of Quantitation (LOQ)	With every initial calibration.	Documented in the specific matrix of concern, at or below the applicable regulatory limit. Equal to lowest calibration standard. At least 3 times the MDL/LOD	Apply J-flag to all results between LOD and LOQ.	
Method Detection Limit (MDL)	A full MDL study is conducted at initial setup and subsequently once per 12-month period and when major changes occur in the method's operating procedures (addition of cleanup procedures, column changes, mobile phase changes). If no changes have been made to the method, quarterly MDL verification checks may be performed in lieu of the yearly MDL study.	MDL study must be performed in the matrix of interest using a standard at a concentration that is 1 to 10 times the estimated MDL value. MDL must be validated through the analysis of a low-level spike at ~ 2 times MDL taken through the entire preparation process. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or re-conduct MDL study.	Samples cannot be analyzed without a valid MDL.

Table 7-F
Quality Control Requirements for Perchlorate by MS Methods (Method EPA 331.0, EPA 332.0, SW6850)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Retention Time (window width calculated for each analyte and internal standard)	At method setup and after major maintenance (e.g., column change).	Width is + 3 times standard deviation for each analyte retention time from 72-hour study.	N/A	N/A
Initial Calibration (ICAL)	Initial calibration prior to sample analysis.	Minimum of 5 calibration standards to establish linearity (daily), r2 > 0.995. The calibration is linear and shall not be forced through the origin.	Correct problem, then repeat initial calibration. Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.
Initial Calibration Verification Standard (ICV)	After initial calibration, daily analysis of a second source standard at the midpoint of the calibration.	%Difference < 15% relative to initial value.	Correct problem and rerun ICV. If that fails, correct problem and repeat initial calibration. Flagging criteria are not appropriate. No samples may be run until calibration has been verified.	Problem must be corrected. No samples may be run until calibration has been verified.
Continuing Calibration Verification Standard (CCV)	Analysis of mid-level standard after every 10 samples. All samples should be bracketed by the analysis of a standard, demonstrating that the system was capable of accurately detecting and quantifying perchlorate.	%Difference < 15% relative to initial value.	Correct problem and rerun CCV and all samples analyzed since last successful CCV. Flagging criteria are not appropriate. No samples may be run until calibration has been verified.	No samples may be analyzed until the problem has been corrected.

Table 7-F
Quality Control Requirements for Perchlorate by MS Methods (Method EPA 331.0, EPA 332.0, SW6850)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Method Detection Limit Verification Standard (MDLV)	Analysis of a standard containing perchlorate at 2 times the MDL concentration. This standard must be analyzed before and directly after every batch of samples is analyzed. It can be analyzed after every 10 samples in order to reduce the reanalysis rate.	Recovery within 30% of its true value.	Correct problem and rerun MDLV and all samples analyzed since last successful MDLV. Flagging criteria are not appropriate. No samples may be run until calibration has been verified.	No samples may be analyzed until the problem has been corrected.
Interference Check Sample (ICS)	Analysis of a standard containing perchlorate at the RL and interfering anions at the concentration determined by the interference threshold study. One ICS is extracted with every batch of 20 samples. It verifies the method performance at the matrix conductivity threshold (MCT). At least one ICS must be analyzed daily.	Monitor recovery of perchlorate and retention time. Recovery within 30%.	Correct problem and then reanalyze all samples in that batch. If poor recovery from the cleanup filters is suspected, a different lot of filters must be used to re-extract all samples in the batch. If column degradation is suspected, a new column must be calibrated before the samples can be reanalyzed.	No samples may be reported that are associated with a failing ICS.

Table 7-F
Quality Control Requirements for Perchlorate by MS Methods (Method EPA 331.0, EPA 332.0, SW6850)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Method Blanks (MB)	One per batch. Undergoes same pretreatment steps as the samples.	< ½ of the RL.	Correct problem, re-prep, then reanalyze method blank and all samples processed with the contaminated blank. If reanalysis fails criteria, flag all positive sample results within 5x the method blank concentration as "J".	
Laboratory Control sample (LCS)	Once per analytical batch spiked at the RL. Undergoes same pretreatment steps as the samples.	Recovery within method requirements or laboratory-generated limits, or 85-115% to verify calibration and to check method performance.	Correct problem, then re-prep and reanalyze the LCS and all associated samples. If corrective action fails, all data should be rejected (flagged as "R")	
Matrix Spikes (MS)	Collect one per 20 samples per matrix, spiked at the RL. Undergoes same pretreatment steps as the samples.	Recovery within 75-125%.	No action is taken based upon MS/MSD data alone. However, using informed professional judgment, the MS/MSD results may be used in conjunction with other QC criteria to determine the need for qualification of the data.	For matrix evaluation only. If MS results are outside the limits, the data must be evaluated to determine the source of the difference and to determine if there is a matrix effect or analytical error.

Table 7-F
Quality Control Requirements for Perchlorate by MS Methods (Method EPA 331.0, EPA 332.0, SW6850)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Matrix Spike Duplicates or Laboratory Duplicates (MS and MSD)	Collect one per 20 samples per matrix, spiked at the RL. Undergoes same pretreatment steps as the samples.	Recovery within MS limits, RPD < 20%.	Flag all positive sample results as "J".	Evaluate the data to determine the source of the difference.
Laboratory Reagent Blank	Analyzed prior to calibration and after samples with over-range concentration of perchlorate and after each batch is analyzed.	Concentration < ½ RL.	Reanalyze reagent blank (until no carryover is observed) and all samples processed since the contaminated blank. Apply J flag to all results not preceded by an acceptable reagent blank if reanalysis is not possible.	
QC Criteria Specific to MS Confirmation				
Mass Tuning	Daily before sample analysis.	Tuning standards should contain the analytes of interest.	Retune instrument. If the tune will not meet acceptance criteria, an instrument mass calibration must be performed and the tuning redone.	Sample analysis should not proceed without an acceptable tuning.
Mass Calibration	Performed prior to sample analysis and calibration curve analysis.	Mass calibration range must bracket the ion masses of interest. The most recent mass calibration must be used and the same mass calibration must be used for all data files in an analytical run. Acceptance criteria must be clearly stated in the laboratory's SOP.	If the mass calibration fails, recalibrate. If it still fails, consult manufacturer instructions on corrective maintenance.	No samples may be analyzed under a failing mass calibration.

Table 7-F
Quality Control Requirements for Perchlorate by MS Methods (Method EPA 331.0, EPA 332.0, SW6850)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Isotope Ratio 35Cl/37Cl	Every sample, spiked sample, and standard and method blank.	Monitor for both the parent ion at mass 99/101 and the product ion at mass 83/85 for MS-MS methods or just 99/101 for MS only. Theoretical ratio ~ 3.06. Must fall between 2.2 to 3.3.	If criteria are not met, sample must be rerun. If sample was not pretreated, sample should be re-extracted using cleanup procedures. If, after cleanup, ratio still fails, use alternative techniques to confirm presence of perchlorate (i.e., a post spike sample, dilution to reduce any interferences, etc.). Data should be qualified as J and should be noted in case narrative.	Decision to report data failing ratio check should be thoroughly documented in case narrative.
Internal Standard (IS)	Addition of 18O-labeled perchlorate to every sample, spiked sample, standard, instrument blank, and method blank.	Measured 18O IS area within + 50% of the value from the initial calibration (retention time window of ~ 0.3% for perchlorate and IS).	Rerun the sample at increasing dilutions until the + 50% acceptance criteria are met. If criteria cannot be met with dilution, the interferences are suspected and the sample must be re-prepped using further pretreatment steps. Data should be qualified as estimated with a J flag and should be discussed in the case narrative.	Use for quantitation and to ensure identification. Failing internal standard should be thoroughly documented in the case narrative.
Interference Threshold Study	At initial setup and when major changes occur in the method's operating procedures (addition of cleanup procedures, column changes, mobile phase changes).	Measure threshold of common suppressors (chloride, sulfate, carbonate, bicarbonate) that can be present in system without affecting quantitation of perchlorate. Threshold is concentration of the common suppressors where perchlorate recovery falls outside of 90-110% window.	N/A	This study and site history will determine the concentration at which the ICS suppressors

Table 7-G
Quality Control Requirements for Total Kjeldahl Nitrogen (TKN) (USEPA Method 351.2 / SM4500)

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/ Flagging Criteria	Comments
Linear Calibration Range using three standards and a blank	every 6 months or significant change in instrument response	$\pm$ 10% linearity	Reestablish linearity, if range shown to be nonlinear, use sufficient standard to clearly define nonlinear portion.	J
Quality Control Sample	At the beginning of test (quarterly), or as required for data-quality	Concentrations $\pm$10% of stated values	Correct problem, reanalyze QCS. Repeat until concentrations within $\pm$ 10% of stated values	J
Method Detection Limit	every 6 months, when a new operator begins work, or significant change in instrument response	-		Flagging criteria not appropriate
Laboratory Reagent Blank	one per batch of samples	< MDL	Correct problem, repeat measurement	J
Laboratory Fortified Blank	one per batch of samples	Recovery between 90-110%	Correct problem, repeat measurement	J
Instrument Performance Check Solution	Checked daily following daily calibration, after every 10^{th} sample, and at the end of sample run	Within 10% of calibration. Peak Gaussian Factor between 0.8 and 1.15 to demonstrate proper instrument performance.	Retention times with a > 2% shift should be investigated and corrected. If column retention time noticeably shifts < 80% from original values, it should be cleaned or replaced.	J
Spike Duplicate	10% of field samples	Recovery between 90-110% 75-125%	Investigate if matrix influences are a factor.	J
Field or Laboratory Duplicate	5% of field samples, or one per sample batch	RPD $\leq$ 25% for aqueous and $\leq$ 50% for solids	Correct problem, repeat measurement	J

Table 8
Surrogate Recovery Limits

Analyte	Water (1)		Soil (2)	
	Lower Control Limit (%)	**Upper Control Limit (%)**	**Lower Control Limit (%)**	**Upper Control Limit (%)**
CLP OLM04.3 VOCs (Multi Level)				
Toluene-d8 (TOL)	88	110	84	138
Bromofluorobenzene (BFB)	86	115	59	113
1,2 dichloroethane-d4 (DCE)	76	114	70	121
CLP OLC03.2 VOCs (Low Concentration)				
Vinyl Chloride-d3	49	138		
Chloroethane-d5	60	126		
1,1-Dichloroethene-d2	65	130		
2-Butanone-d5	42	171		
Chloroform-d	80	123		
1,2-Dichloroethane-d4	78	129		
Benzene-d6	78	121		
1,2-Dichloropropane-d6	84	123		
Toluene-d8	77	120		
trans-1,3-Dichloropropene-d4	80	128		
2-Hexanone-d5	37	169		
Bromoform-d	76	135		
1,1,2,2-Tetrachloroethane-d2	75	131		
1,2-Dichlorobenzene-d4	50	150		
Method 8260B VOCs				
Toluene-d8, 4-bromofluorobenzene, 1,2-dichloroethane-d, and dibromofluoromethane	80-120%		70-130%	
Method 524.2 VOCs				
In-house acceptance criteria or 70-130% when in-house criteria not available				
CLP OLM04.3 SVOCs (Multi Level)				
Nitrobenzene-d5 (Base/Neutral)	35	114	23	120
2-Fluorobiphenyl (Base/Neutral)	43	116	30	115
Terphenyl- d14 (Base/Neutral)	33	141	18	137
Phenol-d5 (Acid)	10	110	24	113
2-Fluorophenol (Acid)	21	110	25	121
2,4,6 Tribromophenol (Acid)	10	123	19	122
2-Chlorophenol- d4 (Acid)	33 (advisory)	110 (advisory)	20 (advisory)	130 (advisory)
1,2-Dichlorobenzened4	16 (advisory)	110 (advisory)	20 (advisory)	130 (advisory)
CLP OLC03.2 SVOCs (Low Concentration)				
Phenol-d5	10	110		
bis-(2-Chloroethyl)ether-d8	41	94		
2-Chlorophenol-d4	33	110		
4-Methylphenol-d8	38	95		

Table 8
Surrogate Recovery Limits

Analyte	Water (1)		Soil (2)	
	Lower Control Limit (%)	**Upper Control Limit (%)**	**Lower Control Limit (%)**	**Upper Control Limit (%)**
Nitrobenzene-d5	35	114		
2-Nitrophenol-d4	40	106		
2,4-Dichlorophenol-d3	42	98		
4-Chloroaniline-d4	8	70		
Dimethylphthalate-d6	62	102		
Acenaphthylene-d8	49	98		
4-Nitrophenol-d4	9	181		
Fluorene-d10	50	97		
4,6-Dinitro-2-methylphenol-d2	53	153		
Anthracene-d10	55	116		
Pyrene-d10	47	114		
Benzo(a)pyrene-d12	54	120		
Method 8270C SVOCs				
phenol-d6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d5, 2-fluorobiphenyl, and p-terphenyl-d14	Laboratory developed limits			
CLP OLM03.2 and OLC03.2 Pesticides/PCBs				
Decachlorobiphenyl	30 (advisory)	150 (advisory)	30 (advisory)	150 (advisory)
Tetrachloro-m-xylene	30 (advisory)	150 (advisory)	30 (advisory)	150 (advisory)
Method 8081A Pesticides				
Decachlorobiphenyl, Tetrachloro-m-xylene	60-150%			
Method 8082A PCBs				
Decachlorobiphenyl, Tetrachloro-m-xylene	70-130%			
SW846 Method 8330				
TBD[(2)]	50	150	50	150

Notes:
(1) For CLP VOC/SVOC/Pesticides/PCB, surrogate recoveries from OLM04.3 (March 2003), Exhibit D. For low concentration level aqueous samples, additional surrogates are required for VOC/SVOC analysis and see specific requirements described in OLC03.2 (December 2000).
(2) Site-specific work plan must specify which surrogate compound is intended.

Table 9-A
LCS Control Limits For Organics
Water Matrix

Analyte	Lower Control Limit (%)	Upper Control Limit (%)
VOCs and SVOCs(CLP and SW846 Methods)	In-house acceptable criteria (70-130% when in-house criteria not available)	
Explosives, SW-846 Method 8330		
1,3,5-Trinitrobenzene	65	140
1,3-Dinitrobenzene	45	160
2,4-Dinitrotoluene	60	135
2,6-Dinitrotoluene	60	135
2,4,6-Trinitrotoluene (TNT)	50	145
2-Amino-4,6-dinitrotoluene	50	155
2-Nitrotoluene	45	135
3-Nitrotoluene	50	130
4-Amino-2,6-dinitrotoluene	55	155
4-Nitrotoluene	50	130
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	50	160
Methyl-2,4,6-trinitrophyenylnitramine (Tetryl)	20	175
Nitrobenzene	50	140
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	80	115
Nitroglycerin	60	120
Pentaerythritol Tetranitrate	60	120

Table 9-B
LCS Control Limits For Organics
Solid Matrix

Analyte	Lower Control Limit (%)	Upper Control Limit (%)
VOCs and SVOCs (CLP and SW846 Methods)	In-house acceptable criteria (70-130% when in-house criteria not available)	
Explosives, SW-846 Method 8330		
1,3,5-Trinitrobenzene	75	125
1,3-Dinitrobenzene	80	125
2,4-Dinitrotoluene	80	125
2,6-Dinitrotoluene	80	120
2,4,6-Trinitrotoluene (TNT)	55	140
2-Amino-4,6-dinitrotoluene	80	125
2-Nitrotoluene	80	125
3-Nitrotoluene	75	120
4-Amino-2,6-dinitrotoluene	80	125
4-Nitrotoluene	75	125
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	70	135
Nitrobenzene	75	125
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	75	125
Nitroglycerin	60	120
Pentaerythritol Tetranitrate	60	120

Table 9-C
LCS Control Limits for Organochlorine Pesticides

CLP OLC03.2 Water Matrix		
Analyte	**Lower Control Limit (%)**	**Upper Control Limit (%)**
4,4'-DDE	50	150
Dieldrin	30	130
Endosulfan sulfate	50	120
Endrin	50	120
gamma-BHC	50	120
gamma-Chlordane	30	130
Heptachlor epoxide	50	150
CLP OLM04.3 SW 846 Method 8081A Water/Soil Matrix		
All analytes	Laboratory advisory limits, or 70~130% when not available	

Notes:
1) For low concentration organic analysis, limits based on Table D-3 from Draft OLC03.0, December 2000.
2) For multi-media, multi-concentration organic analysis, laboratory advisory limits or 70~130% (when laboratory limits not available) will be used in accordance with the USEPA Region 2 SOP for Method 8082.

Table 9-D
LCS Control Limits for Polychlorinated Biphenyls
CLP and SW-846 Method 8082
Water/Soil Matrix

Analyte	**Lower Control Limit (%)**	**Upper Control Limit (%)**
Aroclor 1016	Laboratory advisory limits, or 70~130% when not available	
Aroclor 1260	Laboratory advisory limits, or 70~130% when not available	

Note:
Laboratory advisory limits or 70~130% (when laboratory limits not available) will be used in accordance with the USEPA Region 2 SOP for Method 8082.

Table 9-E
LCS Control Limits for Inorganics
SW-846 Methods 6010B, 6020, 7470A, and 7580
Water Matrix

Analyte	Lower Control Limit (%)	Upper Control Limit (%)
Aluminum	80	120
Antimony	80	120
Arsenic	80	120
Barium	80	120
Beryllium	80	120
Cadmium	80	120
Calcium	80	120
Chromium	80	120
Cobalt	80	120
Copper	80	120
Iron	80	120
Lead	80	120
Magnesium	80	120
Manganese	80	120
Mercury	80	120
Molybdenum	80	120
Nickel	80	120
Potassium	80	120
Selenium	80	120
Silver	80	120
Sodium	80	120
Strontium	80	120
Thallium	80	120
Titanium	80	120
Vanadium	80	120
White Phosphorus	75	125
Zinc	80	120
Zirconium	80	120

Table 9-F
LCS Control Limits for Inorganics
SW-846 Methods 6010B, 6020 and 7471A
Solid Matrix

Analyte	Lower Control Limit (%)	Upper Control Limit (%)
Limits established by USEPA for the LCS		

Table 9-G
LCS Control Limits for Other Analytes

Analyte	Lower Control Limit (%)	Upper Control Limit (%)
Chloride, Sulfate and other Method 300.0 analytes [1]	80	120
Nitrate/Nitrite (Method 353.2) and all other analytes in aqueous [2]	90	110
All other analytes in solids	75, if not specified by Method or SS-WP	125, if not specified by Method or SS-WP

Notes:
1. From Method 300.0.
2. From Method 353.2. The limits are also proposed for all analytes with LCS limits not specified in this SAP or the SS-WP.

Table 10-A
MS/MSD Control Limits for Volatiles

Analyte	Lower Control Limit (%)	Upper Control Limit (%)	RPD%
CLP OLC03.2/OLM04.3 Water Matrix [1]			
1,1-Dichloroethene	61	145	14
Benzene	76	127	11
Trichloroethene	71	120	14
Toluene	76	125	13
Chlorobenzene	75	130	13
CLP OLM04.3 Soil Matrix [2]			
1,1-Dichloroethene	59	172	22
Benzene	66	142	21
Trichloroethene	62	137	24
Toluene	59	139	21
Chlorobenzene	60-	133	21
SW-846 Method 8260B [3] Soil and Water Matrix			
70-130%			

Notes:
1) For CLP water matrix, limits based on Table D-6 from Draft OLC03.0, December 2000 and Table 8 in Exhibit D from OLM04.3, March 2003.
2) For CLP soil matrix, limits based on Table 8 in Exhibit D from OLM04.3, March 2003.
3) For Method 8260B soil and water, limits based on the USEPA Region II SOP for Validating Volatile Organic Compounds by SW-846 Method 8260B, 1999.

Table 10-B
MS/MSD Control Limits for Semivolatiles

Analyte	Lower Control Limit (%)	Upper Control Limit (%)	RPD%
CLP OLC03.2/OLM04.3 Water Matrix [1]			
Phenol	12	110	42
2-Chlorophenol	27	123	40
N-Nitroso-di-n-propylamine	41	116	38
4-Chloro-3-methylphenol	23	97	42
Acenaphthene	46	118	31
4-Nitrophenol	10	80	50
2,4-Dinitrotoluene	24	96	38
Pentachlorophenol	9	103	50
Pyrene	26	127	31
CLP OLM04.3 Soil Matrix [2]			
Phenol	26	90	35
2-Chlorophenol	25	102	50
N-Nitroso-di-n-propylamine	41	126	38
4-Chloro-3-methylphenol	26	103	33
Acenaphthene	31	137	19
4-Nitrophenol	11	114	50
2,4-Dinitrotoluene	28	89	47
Pentachlorophenol	17	109	47
Pyrene	35	142	36
SW-846 Method 8270C [3] Soil and Water Matrix			
In-house generated criteria or 70-130% when in-house criteria not available			

Notes:
1) For CLP water matrix, limits based on Table D-6 from Draft OLC03.0, December 2000 and Table 6 in Exhibit D from OLM04.3, March 2003.
2) For CLP soil matrix, limits based on Table 6 in Exhibit D from OLM04.3, March 2003.
3) For Method 8270C soil and water, limits based on the USEPA Region 2 SOP for Validating Semivolatile Organic Compounds by SW-846 Method 8270, 2001 and Section 9.5.4 from Method 8000C.

Table 10-C
MS/MSD Control Limits for Organochlorine Pesticides/PCBs

Analyte	Lower Control Limit (%)	Upper Control Limit (%)	RPD%
CLP OLC03.2/OLM04.3 Water Matrix [1]			
4,4'-DDT	38	127	27
Aldrin	40	120	22
Dieldrin	52	126	18
Endrin	56	121	21
gamma-BHC	56	123	15
Heptachlor	40	131	20
CLP OLM04.3 Soil Matrix [2]			
4,4'-DDT	23	134	50
Aldrin	34	132	43
Dieldrin	31	134	38
Endrin	42	139	45
gamma-BHC	46	127	50
Heptachlor	35	130	31
SW-846 Method 8081A and 8082A [3] Water and Soil			
In-house generated criteria or 70-130% when in-house criteria not available			

Notes:
1) For water matrix, limits based on Table D-3 from Draft OLC03.0, December 2000 and Table 3 in Exhibit D from OLM04.3, March 2003.
2) For soil matrix, limits based on Table 3 in Exhibit D from OLM04.3, March 2003.
3) For Method 8081A soil and water, limits based on Section 9.5.4 from Method 8000C.

Table 10-D
MS/MSD Control Limits for Inorganics

CLP ILM05.3, ILM06.X, SW 846 Method 6010B and 6020 Water and Soil[1]
75%-125%

Notes:
1) For water matrix, limits based on Table D-3 from Draft OLC03.0, December 2000 and Table 3 in Exhibit D from OLM04.3, March 2003.
2) For soil matrix, limits based on Table 3 in Exhibit D from OLM04.3, March 2003.
3) For Method 8081A soil and water, limits based on Section 9.5.4 from Method 8000C.

Table 10-E
MS/MSD Control Limits for Other Analytes [1]

Water Matrix			
Analyte	**Lower Control Limit (%)**	**Upper Control Limit (%)**	**RPD%**
Chloride, Sulfate and other Method 300.0 analytes	80	120	
Nitrate/Nitrite (Method 353.2)	90	110	
All other analytes for aqueous [2]	90	110	
All other analytes for solids [2]	75	125	

Notes:
1. Limits for LCS specified in the method were used as MS/MSD limits.
2. These limits will be used unless limits are provided by the analytical method or SS-WP.

TABLE 11
Field Equipment Calibration, Maintenance, Testing, and Inspection Summary

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptable Criteria	Corrective Action	Responsible Party	Reference
Horiba U-22 Water Quality Meter Dissolved Oxygen	Manual calibration with 2 standards (zero and saturated)	Replace internal solution (monthly); Clean probes before storage. Replace DO Membrane. Replace Battery		Inspect sponge and replace as necessary (storage)	Morning and Evening	+/- 0.2 mg/L for 0.0 mg/L DO Standard	Replace DO membrane on probe.	Field Team Leader	See Appendix G
Horiba U-22 Water Quality Meter ORP	Manual calibration using standard solution	Replace Battery			Morning and Evening	Within 15 mV of solution	Recalibrate; Replace electrode or have meter inspected	Field Team Leader	See Appendix G
Horiba U-22 Water Quality Meter Temperature	Manual calibration using known temperature standard	Replace Probe; Replace Battery			Morning and Evening	+ / – 2 degrees	Recalibrate	Field Team Leader	See Appendix G
Horiba U-22 Water Quality Meter Conductivity	Auto calibration using a 4 pH standard solution	Replace Battery			Morning and Evening	+ /– 5%	Clean contacts on probe per owners manual	Field Team Leader	See Appendix G
Horiba U-22 Water Quality Meter pH	Auto calibration using a 4 pH standard solution	Replace Battery			Morning and Evening	+ / – 5%	Clean contacts on probe per owners manual; recalibrate with new solution	Field Team Leader	See Appendix G
MiniRae PID	Calibration with 2 points (zero and standard)	Clean PID Lamp and Filter (when zero creeps upward		Inspect filter for dust/foreign objects	Morning and Evening	+/- 2 ppm	Recalibrate	Field Team Leader	See Appendix G

TABLE 11
Field Equipment Calibration, Maintenance, Testing, and Inspection Summary

Field Equipment	Calibration Activity	Maintenance Activity or when in contact with moisture); check battery	Testing Activity	Inspection Activity	Frequency	Acceptable Criteria	Corrective Action	Responsible Party	Reference
Lamotte 2020 Turbidimeter Turbidity	Auto calibration using 2 standard solutions	Replace Lamp Replace Battery Repair	Standard check	Lamp display, battery	Morning and Evening	Display is stable, instrument function normal	Recalibrate, Replace Lamp Replace Battery Repair	Field Team Leader	See Appendix G
HACH Digital Titrator CO_2	Standard Check, Accuracy Check	Replace Reagent	Standard check, accuracy check		Morning and Evening		Rerun standard check	Field Team Leader	See Appendix G
HACH Colorimeter sulfate/sulfied, nitrite, alkalinity	Standard Check, Accuracy Check	Replace battery	Standard check, accuracy check		Morning and Evening		Rerun standard check	Field Team Leader	See Appendix G
HACH Spectrophotometer Ammonia	Calibration with 3 standard solutions	Replace Battery Repair	Standard check, accuracy check		Morning and Evening		Recalibrate, Replace Battery Repair	Field Team Leader	See Appendix G
HACH Hach DR/4000 1-Inch Cell Adapter Manganese	Calibration with 6 standard solutions	Replace Battery Repair	Standard check, accuracy check		Morning and Evening		Recalibrate, Replace Battery Repair	Field Team Leader	See Appendix G
HACH Ferrous iron	Calibration with 4 standard solutions	Replace Battery Repair	Standard check, accuracy check		Morning and Evening		Recalibrate, Replace Battery Repair	Field Team Leader	See Appendix G

Table 12
Performance Criteria for Field Duplicates and Laboratory Duplicates

Laboratory Duplicate		
	Frequency	RPD [1]
Metals (ILM05.3)	One per SDG, or 20 field samples in a SDG, or a group of field samples of a similar concentration level.	20% or CRDL
MEE	One per SDG, or 20 field samples in a SDG, or a group of field samples of a similar concentration level.	20% or RL
VOC/SVOC/Pesticides/PCBs (Matrix Spike Duplicate)	One per SDG, or 20 field samples in a SDG, or a group of field samples of a similar concentration level.	See Table 10
Explosives	One per extraction batch.	20%
Perchlorate	One per SDG, or 20 field samples in a SDG, or a group of field samples of a similar concentration level.	15%
Field Duplicate		
VOC/SVOC/Pesticides/PCBs, TCLP VOC/SVOCs	One every 20 project samples, or per SDG, whichever is more frequent, per matrix	25% (water) 50% (soil)
Metals, TCLP Metals	One every 20 project samples, or per SDG, whichever is more frequent, per matrix	50% or CRDL (water) 100% or CRDL (soil)
MEE	One every 20 project samples, or per SDG, whichever is more frequent, per matrix	25% (water) 50% (soil)
Explosives	One every 20 project samples, or per SDG, whichever is more frequent, per matrix	25% (water) 50% (soil)
Perchlorate, and other analytes	One every 20 project samples, or per SDG, whichever is more frequent, per matrix	25% (water) 50% (soil)

1. Refer to specific USEPA Region 2 SOPs for results close to reporting limits.

Table 13
QC Sample Types and Requirements

Sample Type	Purpose	Collection Requirement
	Field QC Sample	
Field Duplicate	To check reproducibility of laboratory and field procedures. To indicate non-homogeneity.	One every 20 project samples, or per SDG, per matrix
Trip Blank (VOC only)	To check contamination of VOC samples during handling, storage, and shipment from field to laboratory.	One per shipment; to be prepared prior to going into the field except for soil samples (no TB required).
Rinsate Blank	To check field decontamination procedures.	One per sampling event or one per 20 project samples whichever is more frequent, when sampling equipment is decontaminated and reused or when a sample collection vessel will be used..
MS/MSD (Organic Analysis Only)	To check accuracy and precision of organic analyses in specific sample matrices.	One per 20 project samples, generally conducted for samples with relatively high concentrations.
MS (Inorganics)	To check accuracy and precision of inorganic analyses in specific sample matrices.	One per 20 project samples, generally conducted for samples with relatively high concentrations.
	Laboratory QC Sample	
Laboratory QC sample requirement as specified in the specific analytical method.		

Notes:
1. This table presents general QC sample requirement based on previous experience at Seneca and the requirements specified in the following documents:
   (1) NYSDEC. 2001. Development and Review of Site Analytical Plans. March.
   (2) USEPA. 2004. Contract Laboratory Program Guidance for Field Samplers. August.
   (3) USEPA Region 2. 1989. CERCLA Quality Assurance Manual. October.
2. Project-specific QA sample requirement could be derived based on project-specific information; if different from above, the project-specific QA sample requirement should be specified in the SS-WP.

TABLE 14
Inspection/Acceptance Testing Requirements for Consumables and Supplies

Critical Supplies/ Consumables	Inspection/ Acceptance Specifications	Acceptance Criteria	Testing Method	Responsible Party	Handling/ Storage Conditions	Vendor
Isobutylene	Ensure container is pressurized	Visual	Used for PID calibration	Field Team Leader	None specified	Pine Environmental[1]
4 pH standard solution	Inspect for contamination periodically	Visual, or based on poor calibration results	Used for Horiba U-22 Auto calibration	Field Team Leader	None specified	Pine Environmental[1]
Powder for ORP standard solution			Used for Horiba U-22 ORP calibration	Field Team Leader	None specified	Pine Environmental[1]
Sodium hydroxide standard solution	Check fluid monthly for strength	5 – 5.25 mL of solution	Used for CO_2 Hach Titrator	Field Team Leader	None specified	Pine Environmental[1]
Reagent water	Check for evidence of tampering	Visual		Field Team Leader	None specified	Contracted laboratory

Note:
1 – Pine Environmental is the primary vendor used by Parsons for field equipment; other vendors may be utilized for the project.

Table 15
Critical Supplies and Consumables Tracking Log

Tracking Number	Date Received	Meets Inspection/Acceptance Criteria (Y/N, if yes include date)	Retesting Needed (Y/N, if yes include date)	Expiration Date	Initials/Date

Table 16
Sample Handling System

Sample Collection, Packaging and Shipment	
Sample Collection	Field Team
Sample Packing	Field Team
Coordination of Shipment	Field Team Leader
Carrier	Federal Express or UPS - overnight
Sample Receipt and Analysis	
Sample Receipt	Field Analyst / Laboratory
Sample Custody	Field Analyst / Laboratory
Sample Preparation	Field Analyst / Laboratory
Sample Analysis	Field Analyst / Laboratory
Sample Archiving	
Field Sample Storage and Archive	Field Team
Sample Rinse Blanks	Field Team
Sample Trip Blanks	Field Team
Sample Duplicated	Field Team
Sample Disposal	
Sample Disposal	Field Analyst / Laboratory
Storage at Laboratory	Laboratory

Table 17
Summary of Calibration and QC Procedures for Screening Methods [a]

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action [b]	Data Flagging Criteria
USEPA Method 160.3/160.1/ASTM D2216-90/D2216-05	Percent Solids	Field Duplicate	10% of field samples	RPD < 20%	Correct problem, repeat measurement	J
SW846 Method 1010A/1020B/1030	Ignitability	Field Duplicate	10% of field samples	RPD < 20%	Correct problem, repeat measurement	J
SW846 Method 1110	Corrosivity	Duplicate	10% of field samples	RPD < 20%	Correct problem, repeat measurement	J
SW846 Method 9040C with commercially available pH meter	pH (water)	2-point calibration required for each instrument	Once per day	± 0.05 pH units for every buffer	If calibration is not achieved, check meter, buffer solutions, and probe; replace if necessary; repeat calibration	Flagging criteria not appropriate
		pH 7 buffer	At each sample location	± 0.1 pH units	Correct problem, recalibrate	Flagging criteria not appropriate
		Field Duplicate	10% of field samples	± 0.1 pH units	Correct problem, repeat measurement	J
SW846 Method 9045D	pH (soil)	2-point calibration required for each instrument	Once per day	± 0.05 pH units for every buffer	Check with new buffer; if still out, repair meter, repeat calibration check	Flagging criteria not appropriate
		pH 7 buffer	At each sample location	± 0.1 pH units	Recalibrate	Flagging criteria not appropriate
		Field Duplicate	10% of field samples	± 0.1 pH units	Correct problem, repeat measurement. If still out, repeat calibration and reanalyze samples	J

Table 17
Summary of Calibration and QC Procedures for Screening Methods [a]

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action [b]	Data Flagging Criteria
SW846 Method 9050A with commercially available conductivity meter	specific conductance	Calibration with KCl standard	Once per day at beginning of testing	± 5%	If calibration is not achieved, check meter, standards, and probe; repeat calibration	Flagging criteria not appropriate
		Field Duplicate	10% of field samples	± 5%	Correct problem, repeat measurement	J
USEPA Method 130.1	Hardness	Field Duplicate	10% of field samples	Burning rate within ± 10%	Correct problem, repeat measurement	J
USEPA Method 170.1 with commercially available thermometer	Temperature	Field Duplicate	10% of field samples	± 1.0 ˚C	Correct problem, repeat measurement	J
USEPA Method 180.1 with commercially available turbidity meter	Turbidity	Calibration with one formazin standard per instrument range used	Once per day at beginning of test	± 5 units, 0-100 range ± 0.5 units, 0-0.2 range ± 0.2 units, 0-1 range	If calibration is not achieved, check meter; replace if necessary, recalibrate	Flagging criteria not appropriate
		Field Duplicate	10% of field samples	RPD ≤ 20%	Correct problem, repeat measurement	J
E310.1/Hach Method 8203 or similar	Alkalinity	Field Duplicate	10% of field samples	RPD < 20%	Correct problem, repeat measurement	J
E360.1	Dissolved oxygen	Field Duplicate	10% of field samples	RPD < 20%	Correct problem, repeat measurement	J

Table 17
Summary of Calibration and QC Procedures for Screening Methods [a]

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action [b]	Data Flagging Criteria
Organic Vapor Analysis	Hydrocarbon vapor	Samples with elevated readings will be submitted for definitive analysis.				
Hach Methods		In accordance with Hach Method Reference. Field duplicate to be collected for 10% of field samples and RPD should be within 20%.				
ASTM D1498 with commercially available ORP instrument	Oxidation-reduction potential	Sensitivity verification	Daily	ORP should decrease when pH is increased	If ORP increases, correct the polarity of electrodes. If ORP still does not decrease, clean electrodes and repeat procedure.	Flagging criteria not appropriate
		Calibration with one standard.	Daily.	Two successive readings $\pm$10 millivolts	Correct problem, recalibrate	Flagging criteria not appropriate
		Field Duplicate	10% of field samples	$\pm$10 millivolts	Correct problem, repeat measurement	J

Notes:
a. If commercial instrument is used for the analysis, the calibration and QA/QC procedure shall be consistent with the manufacturer's manual or reference.
b. All corrective actions shall be documented, and the records shall be maintained by Parsons.
c. Please refer to SS-WP or specific analytical method for analysis not covered in this table.

Table 18-A. Inorganic Data Qualifier Flags

Data Qualifier	Definition
J	The associated value is an estimated quantity.
UJ	The material was analyzed for, but was not detected. The associated value is an estimate and may be inaccurate or imprecise.
R	The data was unusable. (Note: Analyte may or may not be present.).
U	The material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantitation limit or the sample detection limit.

Table 18-B. Organic Data Qualifier Flags

Data Qualifier	Definition
U	The analyte was analyzed for, but was not detected above the reported sample quantitation limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
N	The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification."
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
UJ	The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Table 19-A

An Example of VOC/SVOC Data Validation Sheet

PROJECT NAME/NO. _____

SDG: _____

LABLORATORY: _____

MEDIA: _____

FRACTION: _____

CRITERIA	Did Analyses Meet all criteria as specified in the SOPS?	If no, specify analysis IDs which do not meet criteria	Comments/Qualifying Actions	Qualifiers Added?
Data Completeness, Holding Times, Preservation, & Solids Percentage				
System Monitoring Compounds				
Matrix Spike/Matrix Spike Duplicates				
Blanks				
GC/MS Instrument Performance Check				
TCL Analytes				
Tentatively Identified Compounds				
Reported Quantitation Limits				
GC/MS Initial Calibration				
GC/MS Continuing Calibration/Calibration Verification				
Internal Standards				
Solids Percentage				
Field Duplicate				

Table 19-B

An Example of Pesticides/PCB Data Validation Sheet

PROJECT NAME/NO. _____
SDG: _____
LABORATORY: _____
MEDIA: _____
FRACTION: _____

CRITERIA	Did Analyses Meet all criteria as specified in the SOPS?	If no, specify analysis IDs which do not meet criteria	Comments/Qualifying Actions	Qualifiers Added?
Data Completeness, Holding Times, Preservation, & Solids Percentage				
System Monitoring Compounds				
Matrix Spike/Matrix Spike Duplicates				
Blanks				
GC Instrument Performance Check				
TCL Analytes				
Reported Quantitation Limits				
GC Initial Calibration				
GC Continuing Calibration/Calibration Verification				
Field Duplicate				

Table 19-C

An Example of Metal Data Validation Sheet

PROJECT NAME/NO. _____
SDG: _____
FRACTION: _____
LABORATORY: _____
MEDIA: _____

CRITERIA	Did Analyses Meet all criteria as specified in the SOPS?	If no, specify analysis IDs which do not meet criteria	Comments/Qualifying Actions	Qualifiers Added?
Data Completeness, Holding Times & Preservation				
Calibration				
Blanks (method blank, prep blank)				
Interference Check Sample				
CRDL Standard				
Laboratory Control Sample				
Duplicates				
Spike Sample Analysis				
ICP Serial Dilution				
Detection Limits				
ICP Linear Range				
Solids Percentage				

Table 20
Summary of Data Validation Criteria [1]

Item	Criteria	Action
Holding Time and Sample Condition	Table 5-A/B of SAP	J data with exceedance, R data if limits grossly exceeded (e.g., exceeding 2 times of holding time).
Blank	No target analyte detected above method detection limit or reporting limit.	See Note 3.
Surrogate	Table 8 of SAP	if recovery>10% and upper limit, J all detects if recovery>10% but below lower limit, J all results if recovery<10%, J detects and R nondetects. [2]
Interference Check Sample (Inorganics Only)	80-120%	J associated detects if recovery is between 121-150%; J all sample results if recovery falls within 50-79%; R sample results for which recovery is less than 50%; R detects if ICS recovery is above 150%.
Instrument Performance Check	GC/MS instrument performance check criteria see specific method.	Professional judgment.
LCS/LCSD	Organics: Laboratory limits (or 70-130% when lab limits not available), others see Table 9 of SAP.	No action for organics based on LCS/LCSD only for organics. For all others, J all associated sample results if below lower limits; J all associated detects if above upper limits. R all data if LCS/LCSD recovery <50%. R all detects if LCS/LCSD recovery>150%.
Matrix Spike	Table 10 of SAP 80-120% (Method 300.0 for sulfate and chloride) 90-110% (Method 353.2 for nitrate and nitrite) 90-110% (all others in aqueous not specified in Method) 75-125% (all others in solids not specified in Method)	No action for organics based on MS/MSD only For all others, J all associated sample results if below lower limits; J all associated detects if above upper limits. [3]
Initial Calibration	CLP VOC/SVOC: %RSD=30%, RRF>=0.05 Method 8260B/8270C: %RSD=15%, RRF>=0.05 Method 524.2: %RSD=20%, RRF>=0.05 Pesticides/PCBs (CLP and SW 846 methods): %RSD=20%, RT within established window. Metals: initial calibration verification recovery within 90~110% (Hg 80~120%, CN 85~115%).	if %RSD>limit, J detects only. if %RSD>90%, R nondetects and J detects if RRF<0.05, R nondetects and J detects. For metals, if recovery > upper limit, J detects only. If recovery is between 75-89% (65-79% for Hg; 70-84% for CN) J all associated results. If recovery is outside the range 75-125% (CN, 70-130%; Hg, 65-135%), reject all associated results. Qualify five samples on either side of verification standard out of limits.
Continuing Calibration	CLP OLM04.3: %D=25%, RRF>0.05 Method 8260B/8270C: %D=20%, RRF>=0.05 CLP OLC03.2 and Method524.2: %D=30%, RRF>=0.05 Pesticides (CLP and SW 846 methods) and PCB (CLP): %D=25%, RT within established window, breakdown of DDT and endrin <=20%, combined breakdown<=30%. PCB (Method 8082): %D=15%, RT within established window. Metals: continuing calibration verification recovery within 90~110% (Hg 80~120%, CN 85~115%).	if %RSD>limit, J detects and UJ nondetects. if %RSD>90%, R nondetects and J detects if RRF<0.05, R nondetects and J detects [2] For metals, if recovery > upper limit, J detects only. If recovery is between 75-89% (65-79% for Hg; 70-84% for CN) J all associated results. If recovery is outside the range 75-125% (CN, 70-130%; Hg, 65-135%), reject all associated results. Qualify five samples on either side of verification standard out of limits.

Table 20
Summary of Data Validation Criteria [1]

Item	Criteria	Action
Contract Required Quantitation Limit Check Standard (Inorganics Only)	80-120%	J all results within affected range (for ICP within 2CRDL from standard, for CN within 50% of standard) if recovery is between 50-79%; J detects within affected range if recovery is between 121-150%; R all data within affected range if recovery is less than 50%; R detects within affected range if recovery is greater than 150%. Qualify 50% of the samples on either side of standard outside limits.
Analyte Results	For analytes measured using GC/MS, relative ion intensities should be consistent with the standards. RRT within 0.06RRT in the corresponding calibration or RT within the established window.	Professional judgment.
Internal Standards (Organics Only)	With the exception of Method 524.2 and CLP OLC03.2, the internal standard area response limits are -50% to +100% of the associated continuing calibration standard. Retention time within 0.50 minutes of internal standard RT for associated calibration. Method 524.2: internal standard recovery within -50% to +100% for each initial mid point calibration and -30% to +100% of the corresponding continuing calibration check. Retention time within 3 standard deviations of the mean retention compounds in the associated initial mid-point calibration standard. CLP OLC03.2: the internal standard area response limits are -40% to +40% of the associated continuing calibration standard. Retention time within 20 seconds of internal standard RT for associated calibration.	if recovery>25% and upper limit, J all detects if recovery>25% but below lower limit, J all results if recovery<25%, J detects and R nondetects. For CLP OLC03.2, see Region 2 SOP for actions. Professional judgment for RT exceedance.
ICP Serial Dilution (Metals Only)	Difference < 10%.	J all associated data for which %D is greater than 10% but less than 100%. R all associated sample results for which %D is greater than or equal to 100%. Qualify only results whose associated raw data are > 10xIDL (or > CRDL when 10xIDL< CRDL)
ICP Linear Range (Metals Only)	All raw sample results within the established ICP linear range.	J all results with associated raw results outside the ICP linear range.
Duplicates	See Table 12 of SAP if not specified, 25% for aqueous and 50% for solids	J the duplicate pair results. Professional judgment for results close to RL. [3]
Solids Percentage	>50%	J detects and UJ nondetects if solids percentage is less than or equal to 50% but greater than 10%. J detects and R nondetects if solids percentage is less than 10%.

Notes:
1. This table is a summary of data validation criteria and action based on the Region 2 SOPs. Refer to Region 2 SOPs (on-line resources available at http://www.epa.gov/region02/qa/documents.htm) for specific analytical method and any methods not included in this table.
2. For SVOCs, pesticides, and PCBs, refer to respective Region 2 SOPs for details.
3. See specific Region 2 SOPs.

Table 21
SAP Distribution List

Personnel Name	Position/Project Title	Organization Name	Telephone Number	Fax Number	E-mail Address
Todd Heino	Program Manager	Parsons	617-449-1405	617-946-9777	todd.heino@parsons.com
Jeff Adams	Task/Project Manager	Parsons	617-449-1570	617-946-9777	jeff.adams@parsons.com
Jackie Travers	Task/Project Manager	Parsons	617-449-1566	617-946-9777	jacqueline.travers@parsons.com
Jim Lowerre	Quality Assurance Officer	Parsons	617-449-1559	617-946-9777	jim.lowerre@parsons.com
David Miller	Senior Customer Service Manager	Severn Trent Laboratories	412-963-7058	412-963-2468	dmmiller@stl-inc.com
Mike Perry/Mark Wilson	Project Manager	Columbia Assurance Services	585-288-5380	585-288-8475	MPerry@rochester.caslab.com MWilson@rochester.caslab.com
Tony Bogolin	Project Manager	Severn Trent Laboratories, Inc., Buffalo	716-691-2600	716-691-7991	tbogolin@stl-inc.com
Bud Gibson	Project Manager	Amerisci Boston	781-337-9334		bgibson@amerisci.com
Tom Andrews	Field Team Leader	Parsons	716-633-7074	716-633-6195	Tom.Andrews@parsons.com
Chunhua Liu	Project Chemist	Parsons	(617) 449-1567	617-946-9777	Chunhua.liu@parsons.com
Julio F. Vazquez	USEPA Region 2 Project Manager	USEPA Region II	212-637-4323	212-637-3256	vazquez.julio@epamail.epa.gov
Kuldeep K. Gupta	NYSDEC Project Manager	NYSDEC	518-402-9620		kxgupta@gw.dec.state.ny.us

Personnel Name	Position/Project Title	Organization Name	Telephone Number	Fax Number	E-mail Address
John Nohrstedt	Project Manager	USACE, Huntsville			John.Nohrstedt@hnd01.usace.army.mil
Keith Hoddinott	Commander	USACHPPM (PROV)	410-436-5209	410-436-5237	Keith.Hoddinott@amedd.army.mil
Chris Boes	Commander	USACE, Aberdeen Proving Grounds	410-436-1513	410-436-1548	Christopher.boes@aec.apgea.army.mil
Edward Kashdan	Contractor for the USEPA	Gannett Fleming, Inc, Audubon, PA	610-650-8101	610-650-8190	
Steve Absolom	BRAC Environmental Coordinator	SEDA	607-869-1309	607-869-1362	stephen.m.absolom@us.army.mil
Randall Battaglia	Project Manager	USACE, NY District	607-869-1523	607-869-1251	randy.w.battaglia@nan02.usace.army.mil
Janet Fallo	Project Manager	USACE, NY District	607-869-1248	607-869-1251	Janet.R.Fallo@nan02.usace.army.mil
Thomas Enroth	Project Manager	USACE, NY District	607-869-1255	607-869-1251	Thomas.R.Enroth@nan02.usace.army.mil
Charlotte Bethoney	Public Health Specialist	Bureau of Environmental Exposure Investigation	518-402-7850		
TBD	Field Subcontractor	TBD	TBD	TBD	TBD

Table 22
RCRA Hazardous Waste Determination Criteria
Seneca Army Depot Activity

Constituent	TCLP Regulatory Level (mg/L)	Equivalent Soil Level (mg/kg)
Arsenic	5.0	100
Barium	100	2000
Benzene	0.5	10
Cadmium	1.0	20
Chloroform	6.0	120
Chromium	5.0	100
1,2-Dichloroethane	0.5	10
1,1-Dichloroethene	0.7	14
2,4-Dinitrotoluene	0.13	2.6
Lead	5.0	100
Mercury	0.2	4
Methyl Ethyl Ketone	200	4000
Selenium	1.0	20
Silver	5.0	100
Tetrachloroethane	0.7	14
Trichloroethane	0.5	10
Vinyl chloride	0.2	4

Table 23
Waste Disposal Classification Criteria
Seneca Army Depot Activity

RCRA Hazardous/ Non-Hazardous	**Contaminated/ Non-contaminated**	**Threat/ No Threat**	**Disposal Option**	**Criteria for Disposal**
Hazardous	Contaminated - Chem	Threat	Off-site	>TCLP
Non-hazardous	Non-contaminated	No threat	On-site	<TCLP, <TAGM
Non-hazardous	Contaminated - Chem	Threat	Off-site	<TCLP, >10XTAGM
Non-hazardous	Contaminated - Chem	No threat	On-site	<TCLP, >TAGM, <10X TAGM
Non-hazardous	Contaminated - Rad	Threat	Off-site: Rad	Uncertain compliance TAGM 4003
Non-hazardous	Contaminated - Chem & Rad	Threat	Off-site: Special Considerations for Radionuclides	> 2X average background

Table 24
UXO Geophysical Investigation Quality Control Frequency and Acceptance Criteria Chart
Seneca Army Depot Activity

Test#	Test Decription	Acceptance Criteria	Power on	Beginning of Day	Beginning & End of Day	1st Day of Project	1 Line per Grid or 100 ft. per Linear Mile
1	Equipment Warm-up	Equipment Specific (typically 5 min)	X				
2	Record Sensor Positions	+/- 1 inch (2.54 cm)		X			
3	Personnel Test	EM61 2mV p-p, Mag 3nT p-p		X			
4	Vibration Test (Cable Shake)	Data Profile does not exhibit data spikes		X			
5	Static Background & Static Spike	Background: EM61 2.5 mV p-p, Mag 1nT p-p			X		
		Spike: +/- 20% of standard item response, after background correction					
6	Azimuthal Text*	Sensor Orientation that minimizes drop-outs				X	
7	Height Optimization	Maximum S/N ratio that reliably detects smallest target objective				X	
8	6 Line Test	Repeatability of response amplitude +/- 20%, Positional Accurancy +/- 20cm				X	
9	Octant Test (Heading Error Test)*	Document heading error for post-processing correction				X	
10	Repeat Data	Repeatability of response amplitude +/- 20%, Positional Accurancy +/- 20cm					X

Note: * Magnetometer Only
Source: USACOE (2002) DID OE-005-05.01.

TABLE 25
EQUIPMENT CHECKLIST FOR CORE SAMPLING

Health and Safety Items
Personnel protective equipment incluidng, but not limited to, the following:
Tyvek
Fulll face respirator and particulate cartridges
Disposable nitrile gloves (powderless)
Latex booties or yellow overboots
Hard hat
Steel-toed boots
Rain gear
Ear plugs
Field first aid kit
Decontamination Items
10 millimeter plastic sheeting
Aluminum foil
Rinse bottles
Alconox
2% Nitric acid
Isopropyl alcohol
Hexane
Paper towels
Deionized water provided by the laboratory
Carboy for potable water
Decontamination tubs (5-gallon buckets)
Long-handled brushes
Deionized water provided by the laboratory for field blanks
Paperwork
Field logbook and black ball point pens
Building Material Sampling Plan with appendices
Daily report forms
Site map
Chain-of-Custody records
Measuring Equipment
Folding ruler marked in tenths of an inch
Sampling Equipment
Pump-up sprayer and distilled water
Distilled Water
Portable coring drill
Diamond tipped coring bits and extensions
Wedge
Hammer
Castor dolly
Wet Vacuum
Food-grade Ziplpoc® bags (1-gallon each)
Packaging and shipping supplies
Clear packing tape
Duct tape
Custody Seals
Bubble wrap
Ice
Ziplpoc® bags (1-gallon each)

TABLE 25
EQUIPMENT CHECKLIST FOR CORE SAMPLING

Miscellaneous
Camera and film (35 millimeter) or digital camera
Flagging
Caution tape
Drum liners
Bung wrench/crescent wrench
Drums

Notes:

Adapted from:

1. Esposito, M., et al., PEI Associates, Inc., and R. Clark, et al., Battelle Bolumbus Laboratories. 1985. *Guide for Decontaminating Buildings, Structures, and Equipment at Superfund Sites,* EPA/600/2-85/028, prepared for the EPA Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, March 1985.
2. OSHA (Occupational Safety and Health Administration). 1979. *Wipe Sampling Policies and Procedures* Chapter VI, OSHA Instruction Manual, CPL 2-20, OSHA Office of Field Coordination, April 1979.

PARSONS

CLIENT/PROJECT TITLE

SENECA ARMY DEPOT ACTIVITY

FINAL GENERIC SITE-WIDE
SAMPLING AND ANALYSIS PLAN

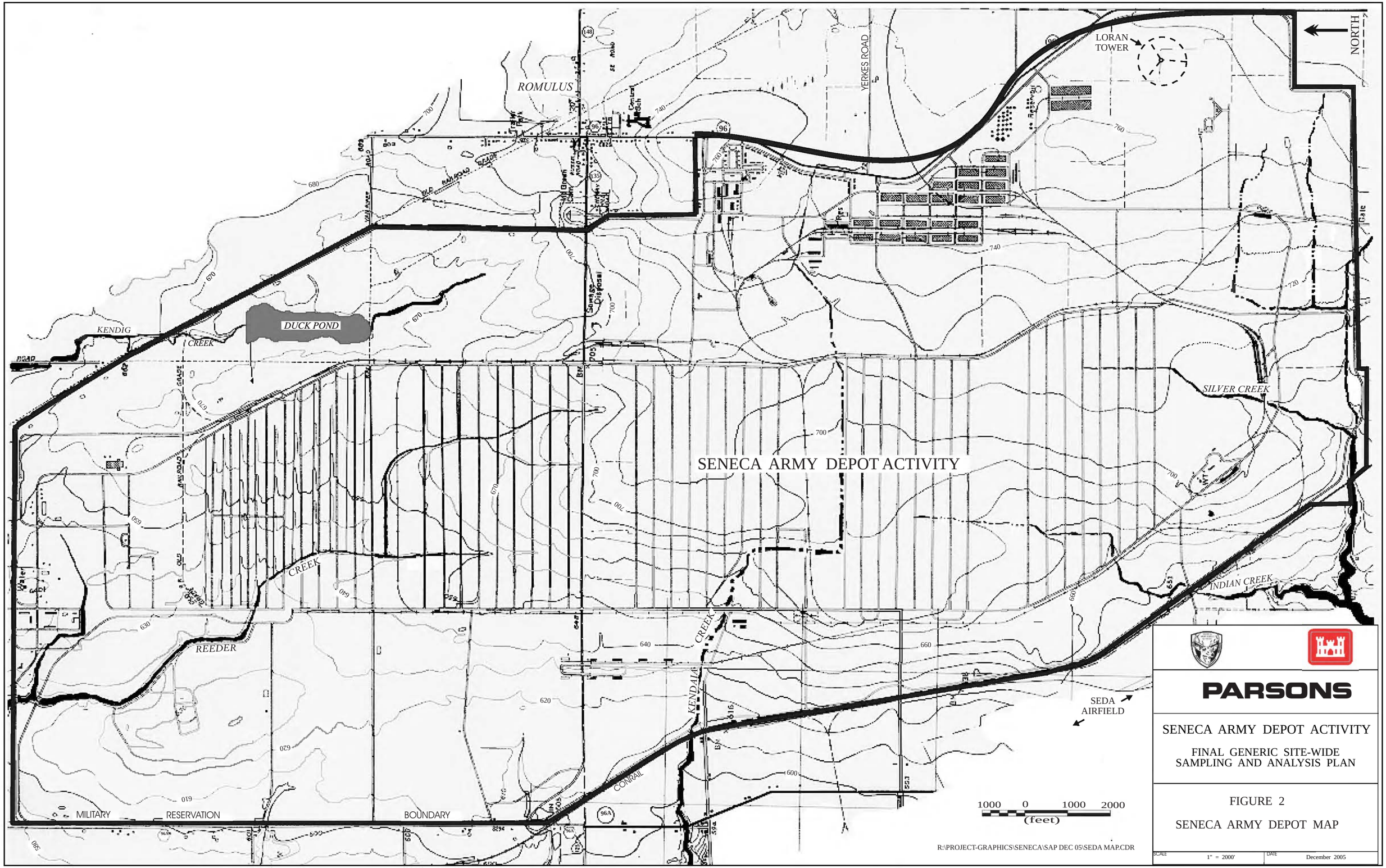
FIGURE 1

LOCATION MAP

SCALE 1 INCH = 8 MILES, APPROX.

DATE December 2005

P:\PIT\Projects\Huntsville HTW\SAP\SAP_DraftFinal\Figures\LOCMAP_SENECA_QAPP.CDR



PARSONS

SENECA ARMY DEPOT ACTIVITY

FINAL GENERIC SITE-WIDE SAMPLING AND ANALYSIS PLAN

FIGURE 2

SENECA ARMY DEPOT MAP

SCALE	DATE
1" = 2000'	December 2005

Figure 3 – Parsons Organization Chart

Seneca Army Depot Activity

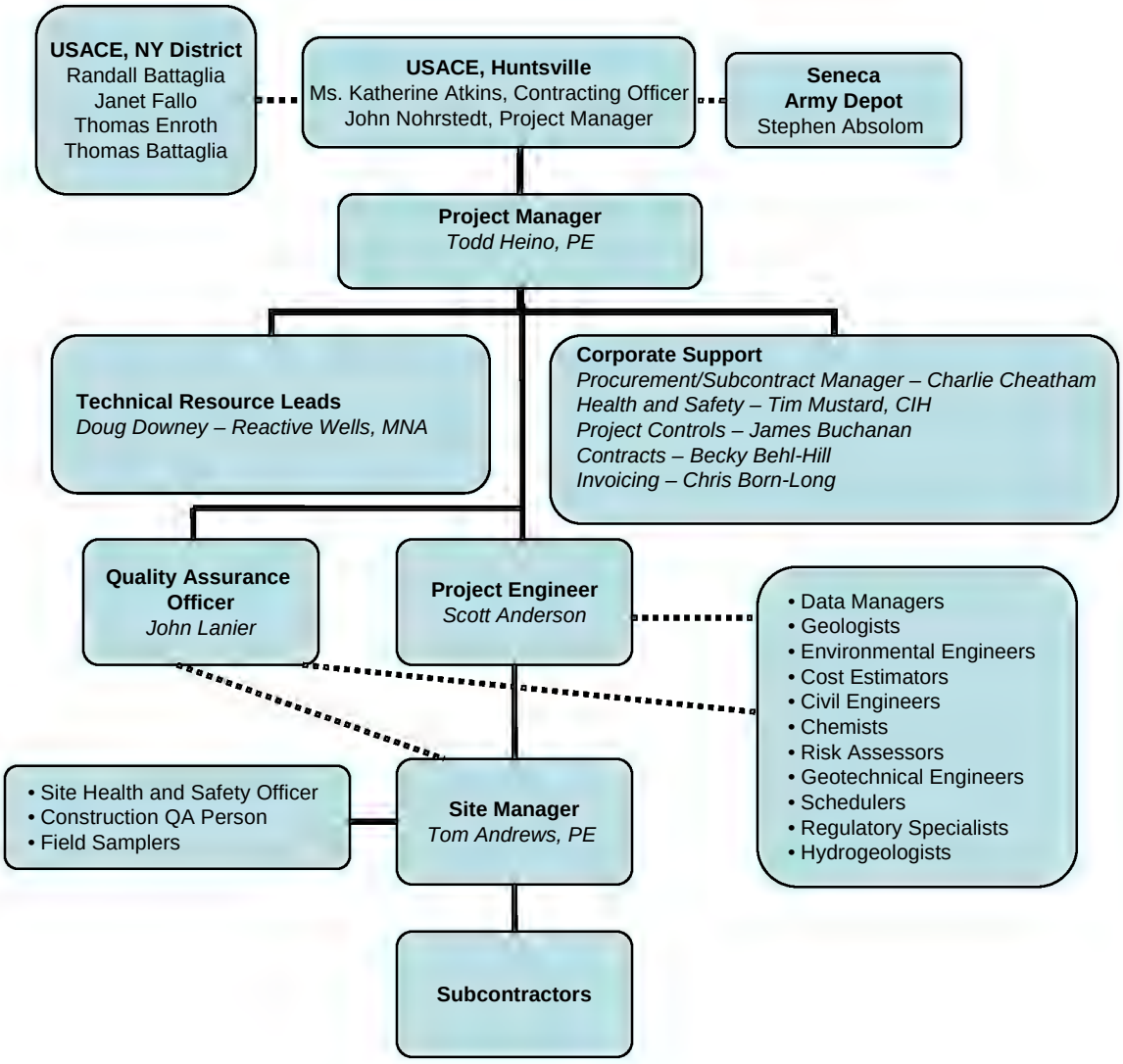


FIGURE 4

INVESTIGATION DERIVED WASTE DISPOSAL FLOW CHART

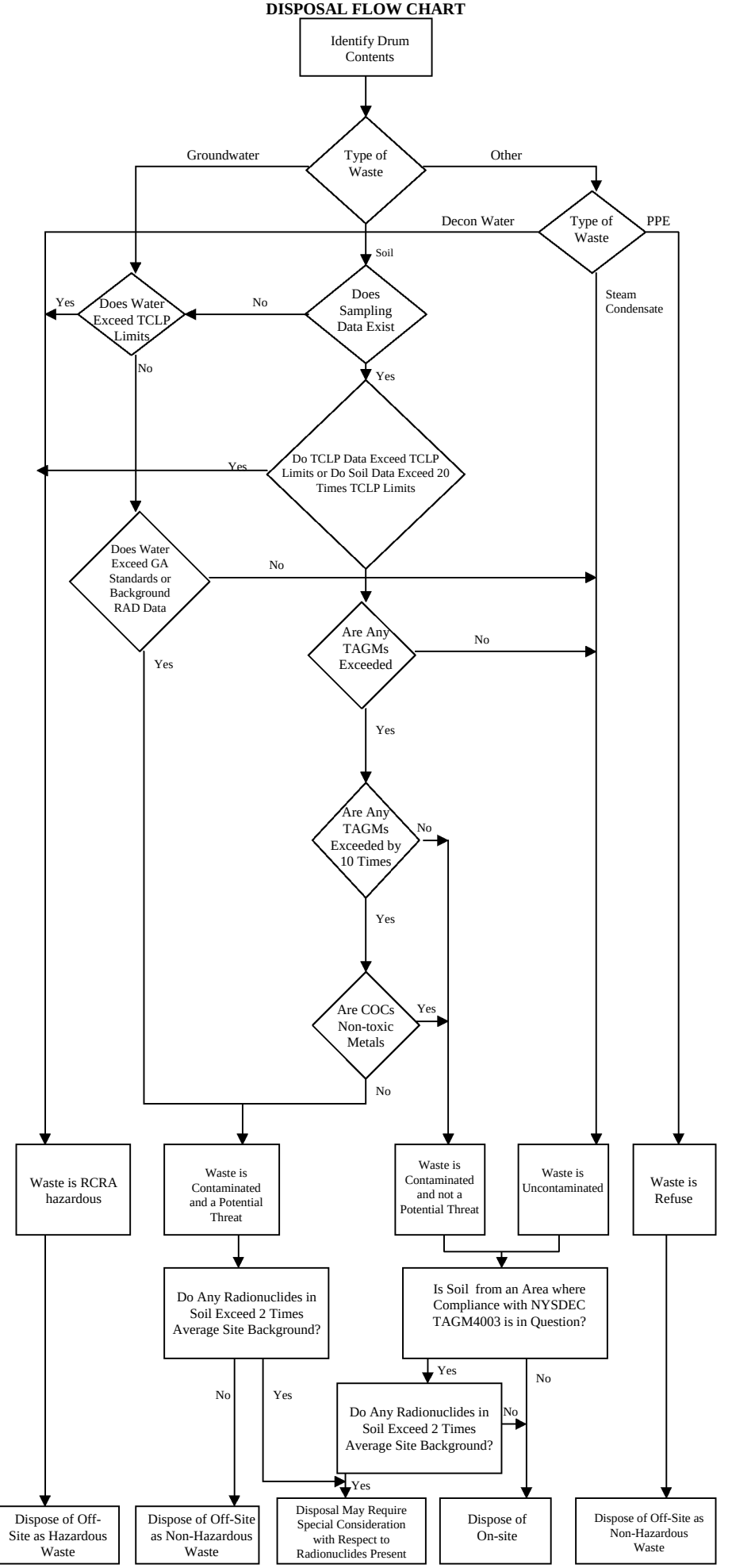
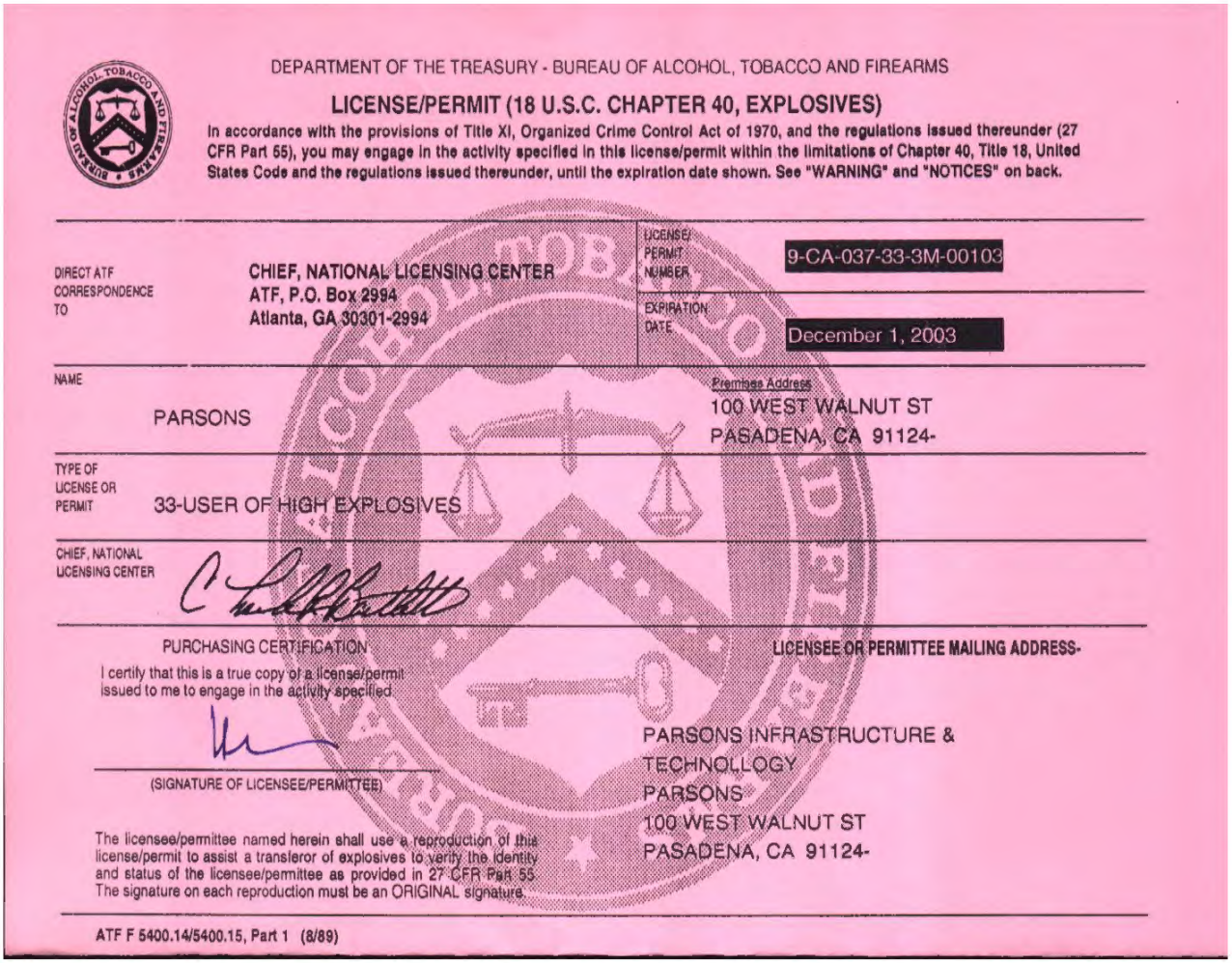


FIGURE 5

PARSONS BATF LICENSE



DEPARTMENT OF THE TREASURY - BUREAU OF ALCOHOL, TOBACCO AND FIREARMS

LICENSE/PERMIT (18 U.S.C. CHAPTER 40, EXPLOSIVES)

In accordance with the provisions of Title XI, Organized Crime Control Act of 1970, and the regulations issued thereunder (27 CFR Part 55), you may engage in the activity specified in this license/permit within the limitations of Chapter 40, Title 18, United States Code and the regulations issued thereunder, until the expiration date shown. See "WARNING" and "NOTICES" on back.

DIRECT ATF CORRESPONDENCE TO: CHIEF, NATIONAL LICENSING CENTER
ATF, P.O. Box 2994
Atlanta, GA 30301-2994

LICENSE/PERMIT NUMBER: 9-CA-037-33-3M-00103

EXPIRATION DATE: December 1, 2003

NAME: PARSONS

Premises Address:
100 WEST WALNUT ST
PASADENA, CA 91124-

TYPE OF LICENSE OR PERMIT: 33-USER OF HIGH EXPLOSIVES

CHIEF, NATIONAL LICENSING CENTER

PURCHASING CERTIFICATION

I certify that this is a true copy of a license/permit issued to me to engage in the activity specified.

(SIGNATURE OF LICENSEE/PERMITTEE)

The licensee/permittee named herein shall use a reproduction of this license/permit to assist a transferor of explosives to verify the identity and status of the licensee/permittee as provided in 27 CFR Part 55. The signature on each reproduction must be an ORIGINAL signature.

LICENSEE OR PERMITTEE MAILING ADDRESS-

PARSONS INFRASTRUCTURE &
TECHNOLLOGY
PARSONS
100 WEST WALNUT ST
PASADENA, CA 91124-

ATF F 5400.14/5400.15, Part 1 (8/89)

Appendix A

Applicable SAP Guidance Cross Reference Table

Appendix A
Applicable SAP Guidance Cross Reference Table
Generic Site-Wide Sampling and Analysis Plan
Seneca Army Depot Activity
Romulus, New York

Section No	Sub-section No.	Title	NYSDEC		USEPA, USEPA Region 2				USACE	
			NYSDEC DER-10	NYSDEC, TAGM SW-96-09	QMP for WED, Appendix 3	EPA QA/R-5	EPA QA/G-5 Region 2 Guidance, 2004	UFP-QAPP, 2005	EM200-1-3	EM200-1-6
		Title and cover				3.2.1 (A1)	A1	2.1	3.3.5.1	
		ACRONYMS							3.3.6	
		Cover Letter				3.2.3 (A3)	A3			
		Header and footer				3.2.2(A2)	A2	2.2.1	3.3.5.2	
		Table of Contents				3.2.2(A2)	A2	2.2.3		
1		Introduction						2.2.4		
2	2.1	Seneca Program Background			Project Management			2.2.4		
	2.2	Project Background			Project Management			2.2.4		
	2.3	Project Scope and Objectives	2.2-1		Project Management			2.5.1		
	2.4	Applicable Regulations								
3		Program Organization and Responsibilities	2.1(a), QAO 2.2-2		Project Management	3.2.4 (A4)	A4	1.3 2.4.1 2.4.2 2.4.3	3.3.5.3 3.3.5.4	
4	4.1	DQO		III-B-1	DQOs	3.2.7 (A7)	A7	2.2.4 2.6.1		
	4.2	Data Types								
	4.3	Data Quality Indicators		III-B-1	DQOs	3.3.5 (B5)	A7	2.6.2	3.3.5.5.2 3.3.5.8	
	4.4	Reporting limits				3.3.7 (B7)		2.6.2 3.2.2	3.3.5.7.2	
	4.5	Quality Control Activities	2.1(b)	III-B-2		3.3.5 (B5)	B5	2.6.2 3.4	3.3.5.7.3	
	4.6	Quality Control Checks				3.3.8 (B8)	B8	2.6.2 3.1.2.5 3.2.4		
5	5.1	Field Sampling Procedure								
	5.2	Sample Collection Documentation						3.3.1		
	5.3	Sample Handling and Custody	2.2-6		Measurement/Data Acquisition	3.3.3 (B3)		3.3.2 3.3.3	3.3.5.6	
6	6	Screening Analytical Methods	2.1(c), 2.1(g)		Measurement/Data Acquisition		B4	3.2.1	3.3.5.7	
7	7	Definitive Data Analytical Methods	2.1(c), 2.1(e), 2.1(h),(i) 2.1(j) 2.1 (k) (l) 2.1(m)		Measurement/Data Acquisition		B4	3.2.1	3.3.5.7	

Appendix A
Applicable SAP Guidance Cross Reference Table
Generic Site-Wide Sampling and Analysis Plan
Seneca Army Depot Activity
Romulus, New York

Section No	Sub-section No.	Title	NYSDEC		USEPA, USEPA Region 2				USACE	
			NYSDEC DER-10	NYSDEC, TAGM SW-96-09	QMP for WED, Appendix 3	EPA QA/R-5	EPA QA/G-5 Region 2 Guidance, 2004	UFP-QAPP, 2005	EM200-1-3	EM200-1-6
8		Data Management			Data Management	3.3.10 (B10)				
	8.1	Data Review Screening Data						3.5.2.1 3.5.4 5.1 5.2.1		
	8.2	Data Review Definitive Data	2.1(d), 2.1(f)			3.2.9 (A9)	D1	3.5.2.3 3.5.3 3.5.4 5.1 5.2.1	3.3.5.9 3.3.5.10.2	2-1 2-3 2-4 3-1 3-3
	8.3	Data reduction			Data Management		B3	3.5.4	3.3.5.8	
	8.4	Data assessment procedure						5.1 5.2	3.3.5.10.1	
	8.5	Data Verification			Data Management					
	8.6	Data Validation			Data Validation and usability	3.5.1 (D1) 3.5.2 (D2) 3.5.3 (D3)	D2	3.5.4 5.1 5.2.2	3.3.5.10.2 3.3.5.10.4	3-1 3-3
	8.7	Data Usability Assessment						5.2.3		
	8.8	Non-direct Measurement Data Evaluation					B9	2.7		
	8.9	Reconciliation					D3		3.3.5.10.3	
	8.10	Electronic data reports	2.2-7			3.2.9 (A9)		3.5.3	3.3.5.9	2-2
	8.11	Data Tracking and Archiving			Data Management			3.5.4 3.5.5	3.3.5.9	
	8.12	Hardcopy data reporting format						3.5.3	3.3.5.9	2-2
	8.13	Data Analysis						3.5.4		
9		Performance and Audits			Assessment/Oversight	3.3.6 (B6) 3.4.1 (C1)	C1	4.1.1 4.1.2	3.3.5.7.4	
10		Preventive Maintenance				3.3.6 (B6)	B7	3.1.2.4 3.2.3	3.3.5.7.1	
11		Nonconformance/Corrective Actions						1.2.7 4.1.2	3.3.5.7.5	
12		QA Reports to Management			QA Reports	3.2.9 (A9)	C2	4.2		4
13		Revisions and Distribution			Updates and Revision	2.7 3.2.9 (A9) 3.2.3 (A3)	A3	1.2.7 1.2.8 2.2.2 2.3.1 2.3.2	3.3.5.2	

Appendix A
Applicable SAP Guidance Cross Reference Table
Generic Site-Wide Sampling and Analysis Plan
Seneca Army Depot Activity
Romulus, New York

Section No	Sub-section No.	Title	NYSDEC		USEPA, USEPA Region 2				USACE	
			NYSDEC DER-10	NYSDEC, TAGM SW-96-09	QMP for WED, Appendix 3	EPA QA/R-5	EPA QA/G-5 Region 2 Guidance, 2004	UFP-QAPP, 2005	EM200-1-3	EM200-1-6
14		Special Training/Certification				3.2.8 (A8)	A8	2.4.4		
15		Documents and Records				3.2.9 (A9)	A9	1.2.8 3.5.1		
16		Field Sampling Plan	2.2-3, 2.2-6,	III-B-3	Measurement/Data Acquisition	3.3.2 (B2)		3.1.2 3.3.2 3.4 Appendix A, SOP	3.3.4	
17		Site-Specific Work Plan Requirements	2.2-4, 2.2-5,	III-B-2	Measurement/Data Acquisition	3.2.5 (A5) 3.2.6 (A6) 3.3.4 (B4) 3.3.5 (B5)	A7 A8 B1 B2 B9 D3	2.5 - 2.8 3.1.1 3.4	3.3.5.5.1	
18		References								
Figure 3		Organization Chart				A4	A4	1.3 2.4.1	3.3.5.3 3.3.5.4	
Tables						3.3.2 (B2) 3.3.5 (B5)	B2 B3	2.4.2 3.1.2.2 3.2 3.4	3.3.5.7	
Appendix A		Cross Reference table					A2			
Appendix E		Sign-Off Sheet						2.3.2		

References:
1. NYSDEC. 2002. Draft DER-10. Technical Guidance for Site Investigation and Remediation
2. NYSDEC. 2001. Technical Administrative Guidance Memorandum SW-96-09. Development and Review of Site Analytical Plans.
3. USEPA. 2001. Quality Management Plan for Western Ecology Division.
4. USEPA. 2001. EPA Requirements for Quality Assurance Project Plans. EPA QA/R-5.
5. USEPA. 2002. Guidance for Quality Assurance Project Plans. EPA QA/G-5.
6. USEPA Region 2. 2004. Guidance for the Development of Quality Assurance Project Plans for Environmental Monitoring Projects.
7. USEPA. 2005. Uniform Federal Policy for Quality Assurance Project Plans. May
8. USACE. 2001. Requirements for the Preparation of Sampling and Analysis Plans. EM200-1-3.
9. USACE. 1997. Chemical Quality Assurance for Hazardous, Toxic and Radioactive Waste (HTRW) Projects. EM200-1-6.

Appendix B

NYSDEC Analytical Service Protocol (ASP)

EXHIBIT A

SUMMARY OF REQUIREMENTS

Exhibit A

Table of Contents

Exhibit A

Table of Contents

Section I - General Requirements

The Laboratory shall use proven instruments and techniques to identify and measure the concentrations of a variety of environmental parameters listed in Exhibit C. The Laboratory shall employ state-of-the-art analytical procedures to perform all analyses specified by the Contract Lab Sample Information Sheet (Figure #1 attached), including all necessary preparations for analysis.

1.0 Purpose

The New York State Department of Environmental Conservation (NYSDEC) in 1980 implemented a program to obtain analytical services from private analytical laboratories. The purpose of the program is to provide analytical data for use by NYSDEC in support of its investigation, clean-up, and monitoring activities under the Clean Water Act, the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA). In support of this program NYSDEC has developed this multi-media, multi-concentration Analytical Service Protocol (ASP).

2.0 Description of Service

The ASP provides a framework for laboratories to apply various USEPA analytical methods for the isolation, detection, and quantitative measurement of target compounds in water, soil/sediment, tissue, and hazardous waste environmental samples. The ASP provides methods that may be used, and the specific quality control and reporting requirements by which the laboratory will generate the data. This service uses a wide variety of analytical methods to analyze the target compounds.

3.0 Data Uses

This analytical service provides data which NYSDEC uses for a variety of purposes, such as determining the nature and extent of contamination at a hazardous waste site, assessing priorities for response based on risks to human health and the environment, determining appropriate cleanup actions, determining when remedial actions are complete, and determining compliance with regulatory permit limits and environmental standards. The data may be used in all stages in the investigation of a hazardous waste site, including site inspections, Hazard Ranking System scoring, remedial investigations/feasibility studies, remedial design, treatability studies, and removal actions. In addition, this service provides data that are available for use in enforcement/litigation activities.

4.0 Summary of Requirements

4.1 Introduction to the ASP. The ASP is designed as part of the documentation for a contract between NYSDEC and a commercial laboratory performing analyses in support of NYSDEC programs. The ASP is comprised of eight exhibits. Exhibit A provides an overview of the ASP and its general requirements. Exhibit B contains a description of the reporting and deliverables requirements, in addition to the data reporting forms and the forms instructions. Exhibit C specifies the target compound list for this ASP with the contract-required quantitation limits for

sample matrices. Exhibit D details the specific analytical procedures to be used with this ASP and resulting contracts. Exhibit E provides descriptions of required quality assurance/quality control (QA/QC), standard operating procedures, and procedures used for evaluating analytical methodologies, QA/QC performance, and the reporting of data. Exhibit F contains chain-of-custody and sample documentation requirements, which the Laboratory shall follow. To ensure proper understanding of the terms utilized in this ASP, a glossary can be found in Exhibit G (when a term is used in the text without explanation, the glossary meaning shall be applicable). Specifications for reporting data in computer-readable form appear in Exhibit H.

4.1.1 Exhibit D provides the Laboratory with the specific analytical procedures to be used and defines the specific application of these procedures to this contract. The procedures described are a compilation of methods required by several different monitoring programs and activities. The Laboratory shall utilize the appropriate program specified procedures for the analysis of each sample, based on information contained on the Contract Lab Sample Information Sheet. These procedures include instructions for sample preparation, screening, identification, quantification, and data evaluation. Where appropriate, specific ions used for searching the mass spectral data for each compound are included. The Laboratory shall perform sample preparation and analysis procedures as prescribed in Exhibit D, while meeting specified sample preservation and holding time requirements as specified in Exhibit I.

4.1.2 The Laboratory shall prepare necessary extracts, digestates, and dilutions of samples. The Laboratory shall screen organic extracts by methods of its choice (soil characterization mandatory; water characterization optional) at an initial extract concentration. Then, based on the screening response, the Laboratory shall use the specific analytical methods described in Exhibit D to extract and concentrate samples to achieve the Contract Required Quantitation Limits (CRQL) listed in Exhibit C. Exhibit D lists the analytical methods and starting points to be achieved for each parameter.

4.1.3 The Laboratory shall adhere to the quality assurance/quality control requirements specified in Exhibit E for all samples analyzed under this protocol.

4.1.4 During organic preparation, the Laboratory shall fortify all samples, blanks, matrix spikes, and matrix spike duplicates with the appropriate surrogate spiking compounds listed in Exhibits D and E. Additionally, all sample semivolatile extracts and aliquots for volatile organics analysis shall be spiked with the internal standard compounds listed in Exhibits D and E before injection or purging.

4.1.5 Additionally, for each sample analyzed by GC/MS, the Laboratory shall conduct mass spectral library searches to determine the possible identity of up to ten (10) volatile components and up to twenty (20) semivolatile components that are neither system monitoring compounds, surrogates, internal standards, or on the program specific volatile or semivolatile Target Compound List (TCL) (Exhibit C).

4.1.6 Exhibit F contains chain-of-custody and sample documentation requirements that the Laboratory must follow in processing samples under this

Protocol, and specifies requirements for written laboratory standard operating procedures.

4.1.7 Sample analysis, sample documentation, and other deliverables shall be reported as specified in Exhibit B. Specifications for reporting data in computer-readable format appear in Exhibit H.

4.1.8 To ensure proper understanding of language utilized in this Protocol, Exhibit G contains a glossary of terms. When a term is used in the text without explanation, the glossary meaning shall be applicable. Glossary definitions do not replace or take precedence over specific information included in the Protocol text.

4.1.9 The samples to be analyzed by the Laboratory may be from known or suspected hazardous waste sites and, potentially, may contain hazardous organic and/or inorganic materials at high concentration levels. The Laboratory should be aware of the potential hazards associated with the handling and analyses of these samples. It is the Laboratory's responsibility to take all necessary measures to ensure the health and safety of its employees.

4.1.10 In addition, the Laboratory must be aware of the importance of maintaining the integrity of the data generated under the Protocol as it is used to make major decisions regarding public health and environmental welfare. In addition, it may be used in litigation against potentially responsible parties in the enforcement of Superfund legislation.

4.1.11 In the vast majority of shipments, samples will be delivered directly to the laboratory facility by overnight delivery service. However, in the infrequent instance that it is necessary, the Laboratory shall be responsible for any handling or processing required for the receipt of sample shipments, including pickup of samples at the nearest servicing airport, bus station, or other carrier service within the laboratory's geographical area. The Laboratory shall pick up sample shipments within twenty-four (24) hours of notification.

4.1.12 Various Divisions within NYSDEC to fulfill workplan or consent order requirements may use any and all methods contained within this Protocol for direct contracting of laboratory services.

4.1.13 The Laboratory shall prepare sample containers in accordance with the specifications in Exhibit I, unless specifically directed to do otherwise by the Bureau of Watershed Assessment and Research (BWAR) or the Project Officer (PO).

74-15-1 (9/97)—q One Copy of This Sheet Goes To: a) Room 392, 50 Wolf Road, Albany, New York 12233-3502
b) With sample to contract lab c) Retain for your records

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

CONTRACT LAB SAMPLE INFORMATION SHEET

Print Legibly

CAUTION (check if applicable)

Lab personnel are expected to use caution when handling DEC samples, however, please use special caution when handling this sample since it is believed to contain significant concentrations of hazardous and/or toxic material(s).

CHECK THE BOX PRECEDING THE REQUESTED ANALYSIS

PRIORITY POLLUTANTS (Water Part 136)—SPDES

2. 13PP Metals	3. Volatiles—(USEPA 624 GC/MS)	6. Pesticides/PCBs (USEPA 608-GC)
4. Acids Base/Neutrals (USEPA 624 GC/MS)	5. Cyanide	9. BOD
7. Halogenated Volatiles (USEPA 601 GC)	8. Aromatic Volatiles USEPA 602 GC)	12. TSS
10. pH	11. COD	15. Ammonia
13. Settleable Solids	14. TKN	18. Reactive Phosphorus
16. Nitrate/Nitrite	17. Total Phosphorus	21. Total Phenols
19. Oil/Grease	20. TOC	60. PCBs congener method (ASP 91-11)
22. Other _____	59. PCBs at 0.065 Φg/l	64. Total Solids
	62. CBOD	65. Volatiles (USEPA 524.2 GC/MS)

CONTRACT LABORATORY PROTOCOLS

23. (ALL)—Water—Includes 24-28	29. (ALL)—Soil/Sediments—Includes 30-34
24. Base/Neutral/Acid (B/N/A)—GC/MS (ASP #95-2)	30. (B/N/A)—Soil/Sediments—GC/MS (ASP #95-2)
25. Volatile Organic Analysis VOA—Water—GC/MS (ASP #95-1)	31. VOA—Soil/Sediments—GC/MS (ASP #95-1)
26. Pesticides/PCBs—Water—GC/MS (ASP #95-3)	32. Pesticides/PCBs—Soil/Sediments—GC (ASP #95-3)
27. Metals—23 in Water	33. Metals—23 in Soil/Sediments
28. Cyanide—Water	34. Cyanide—Soil/Sediments
66. Dioxin-Water (ASP #91-7)	67. Doixin-Soil/Sediments (ASP #91-7)
35. Other _____	

HAZARDOUS WASTES/RCRA ANALYSIS SW-846

36. EP Toxicity	37. EP Toxicity (Metals Only)	38. Ignitability
39. Corrosivity	40. VOA—(USEPA 8260 GC/MS)	41. BNA—(USEPA 8270 GC/MS)
42. Pesticides/PCBs (USEPA 8081)	43. TCLP	44. TCLP (Metals Only)
45. Reactivity	46. Dioxin (USEPA 8280)	47. Appendix IX
48. Other	63. Percent Solids	68. Metals—17 Hazardous

MUNICIPAL SLUDGE

56. RS-01 57. RS-01 58. Other _____

COLLECTED BY:	TELEPHONE NUMBER:	REGION NO.:

CONTRACT LABORATORY:	COUNTY:	SAMPLING DATE:	MILITARY TIME:

SAMPLE MATRIX:

Air Soil/Sediment Groundwater Surface Water Wastewater Other _____

CASE NO.	SDG NO.	SAMPLE NO.	CHECK FOR MS/MD	TYPE OF SAMPLE
			This Sample	Grab Composite Term _____ hours

Check if there will be more samples with this SDG sent in this calendar week.

SAMPLING POINT:

Report via Category B, unless checked

Check if field duplicate | Outfall Number

Check if sampling is part of inspection

FLOW: _____ GPD _____ MGD

SPDES NUMBER/REGISTRY NUMBER

Figure #1 - Contract Lab Sample Information Sheet

Figure #2 - Sample Invoice

LABORATORY NAME: _____ INVOICE # _____
ADDRESS: _____ DATE: _____
CITY/STATE/ZIP: _____

Invoice to:
NYSDEC
50 Wolf Road, Rm. 392
Albany, NY 12233-3502

Remit to:
LABORATORY NAME
ADDRESS (If different from above)
CITY/STATE/ZIP

Contract # _____ Fed. I.D. # _____

_____

LAB I.D. # / CASE #/SDG #/SAMPLE # / MATRIX	ANALYSIS	PRICE
nnnnnnn		
E900/00030/1234-01	13 PP Metals	$
Wastewater	Volatiles (624)	$
	B/N/A (625)	$
	CN	$
	Pest/PCB (608)	$
nnnnnnn		
E900/00030/1234-02	BOD	$
Wastewater	TSS	$
	TKN	$
	NH3	$
nnnnnnn		
E900/00030/1234-03	O/G	$
Wastewater	Tot. Phenols	$
nnnnnnn-QC		
E900/00030/1234-MS	13 PP Metals	$
	Volatiles (624)	$
	B/N/A (625)	$
	CN	$
	Pest/PCB (608)	$
nnnnnnn-QC		
E900/00030/1234-MSD	13 PP Metals	$
	Volatiles (624)	$
	B/N/A (625)	$
	CN	$
	Pest/PCB (608)	$
	TOTAL AMOUNT	$

4.1.14 Invoices for work performed under this Protocol as a direct analytical services contractor to NYSDEC **MUST** be submitted in the **EXACT** format shown in the example in Figure # 2 following. Invoices not in this format will be returned to the Laboratory for resubmission.

4.1.15 Prior to accepting any samples from the NYSDEC, the Laboratory shall have, in-house, the appropriate standards for all target compounds listed in Exhibit C.

4.2 Overview of Major Task Areas. For each sample, the Contractor shall perform the tasks described in this section. Specific requirements for each task are detailed in the exhibits as referenced.

4.2.1 Task I: Chain-of-Custody

4.2.1.1 Chain-of-Custody. The Laboratory shall receive and maintain samples under proper chain-of-custody procedures. All associated document control and inventory procedures shall be developed and followed. Documentation, as described therein, shall be required to show that all procedures are being strictly followed. This documentation shall be reported as the Complete Sample Delivery Group File (CSF) (see Exhibit B). The Laboratory shall establish and use appropriate procedures to handle confidential information received from the Agency. See Exhibit F for specific requirements.

4.2.1.2 Sample Scheduling/Shipments. Sample shipments to the Laboratory's facility will be scheduled and coordinated by the NYSDEC Bureau of Watershed Assessment and Research (BWAR) and or the Project Officer (PO). The Laboratory shall communicate with BWAR/PO personnel by telephone, as necessary throughout the process of sample scheduling, shipment, analysis, and data reporting, to ensure that samples are properly processed. At the time of sample scheduling, the Laboratory will be notified if the Modified SW-846 Method 5035 is to be used in the preparation and analysis of low level soil samples for volatiles.

4.2.1.2.1 Samples will be shipped routinely to the Laboratory through an overnight delivery service. However, as necessary, the Contractor shall be responsible for any handling or processing required for the receipt of sample shipments, including pick-up of samples at the nearest servicing airport, bus station, or other carrier service within the Laboratory's geographical area. The Laboratory shall be available to receive sample shipments at any time the delivery service is operating, including Saturdays.

4.2.1.2.2 If there are problems with the samples (e.g., mixed media, containers broken or leaking) or sample documentation/paperwork (e.g., Contract Laboratory Sample Information Sheets (CLSIS) not with shipment, sample and CLSIS numbers do not correspond), the Laboratory shall immediately contact BWAR/PO for resolution. The Laboratory shall immediately notify BWAR/PO regarding any problems and laboratory conditions that affect the timeliness of analyses and

data reporting. In particular, the Laboratory shall notify BWAR/PO personnel in advance regarding sample data that will be delivered late and shall specify the estimated delivery date.

4.2.1.2.3 To effectively monitor the temperature of the sample shipping cooler, NYSDEC may include a sample shipping cooler temperature blank with each cooler shipped. The temperature blank will be clearly labeled: NYSDEC COOLER TEMPERATURE INDICATOR.

4.2.1.2.3.1 When the NYSDEC supplies a cooler temperature indicator bottle in the sample shipping cooler, the Laboratory shall use the NYSDEC supplied cooler temperature indicator bottle to determine the cooler temperature. The Laboratory shall measure the temperature of the cooler at the time of sample receipt.

4.2.1.2.3.2 The temperature of the sample shipping cooler shall be measured and recorded immediately upon opening the cooler, and prior to unpacking the samples or removing the packing material.

4.2.1.2.3.3 To determine the temperature of the cooler, the Laboratory shall locate the cooler temperature indicator bottle in the sample shipping cooler, remove the cap, and insert a calibrated thermometer into the cooler temperature indicator bottle. Prior to recording the temperature, the Laboratory shall allow a minimum of 3 minutes, but not greater than 5 minutes, for the thermometer to equilibrate with the liquid in the bottle. At a minimum, the calibrated thermometer (±1°C) shall have a measurable range of 0 to 50 degrees Celsius. Other devices which can measure temperature may be used if they can be calibrated to ±1°C and have a range of 0 to 20°C. If a temperature indicator bottle is not present in the cooler, an alternative means of determining cooler temperature shall be used. However, under no circumstances shall a thermometer or any other device be inserted into a sample bottle for the purpose of determining cooler temperature. The Laboratory shall contact BWAR/PO and inform them that a temperature indicator bottle was not present in the cooler. The Laboratory shall document the alternative technique used to determine cooler temperature in the SDG Narrative.

4.2.1.2.3.4 If the temperature of the sample shipping cooler's temperature indicator exceeds 10 degrees Celsius, the Laboratory shall

contact BWAR/PO, inform them of the temperature deviation, and obtain instructions on how to proceed. The BWAR/PO will either require that no sample analysis(es) be performed or that the Laboratory proceed with the analysis(es). The Laboratory shall document the BWAR/PO decision in the SDG Narrative. Also in the SDG Narrative, the Laboratory shall list by fraction, the NYSDEC sample number of all samples, which were shipped in a cooler, which exceeded 10 degrees Celsius.

4.2.1.2.3.5 The Laboratory shall record the temperature of the cooler on the DC-1 Form, under Remark # 9 - Cooler Temperature, and in the SDG Narrative.

4.2.1.2.4 The Laboratory shall accept all samples scheduled by BWAR/PO, provided that the total number of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Laboratory elect to accept additional samples, the Laboratory shall remain bound by all contract requirements for analysis of those samples accepted.

4.2.1.2.5 The Laboratory shall be required to routinely return sample shipping containers (e.g., coolers) to the appropriate sampling office within 14 calendar days following shipment receipt (see Clause entitled Government Furnished Supplies and Materials).

4.2.2 Task II: Analysis of Samples

4.2.2.1 Overview. - Sample analyses will be scheduled by groups of samples, each defined as a SDG and identified by a unique NYSDEC Case and SDG number assigned by BWAR. A Case number identifies to NYSDEC fiscal personnel the funding source that will be used in processing the sample invoice. An SDG signifies a group of samples collected at one site or geographical area over a finite time period, and will include one or more field samples with associated blanks. Samples may be shipped to the Laboratory in a single shipment or multiple shipments over a period of time, depending on the size of the SDG.

4.2.2.1.1 A Sample Delivery Group (SDG) is defined by the following, whichever is most frequent:

Each cooler of field samples received, OR

Each 20 field samples (excluding PE samples) within an SDG, OR

Each 7 calendar day period (excluding Sundays and Government holidays) during which field samples in an SDG are received (said period beginning with the receipt of the first sample in the SDG).

4.2.2.2 Preparation Techniques. The Laboratory will prepare samples as described in Exhibit D. For semivolatile and pesticide/Aroclor samples, an aliquot is extracted with a solvent and concentrated. The concentrated extract is subjected to fraction-specific cleanup procedures and then analyzed by GC/MS for semivolatile or GC/EC for the pesticide/Aroclor target compounds listed in Exhibit C. For volatile samples, an aliquot is purged with an inert gas, trapped on a solid sorbent, and then desorbed onto the GC/MS for analysis of the target compounds listed in Exhibit C.

4.2.2.3 Analytical Techniques. The target compounds listed in Exhibit C shall be identified as described in the methodologies given in Exhibit D. Automated computer programs may be used to facilitate the identification of compounds.

4.2.2.4 Qualitative Verification of Compounds. The volatile and semivolatile compounds identified by GC/MS techniques shall be verified by an analyst competent in the interpretation of mass spectra by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. This procedure requires the use of multiple internal standards.

4.2.2.4.1 If a compound initially identified by GC/MS techniques cannot be verified, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the Laboratory shall report that identification and proceed with quantitation.

4.2.2.4.2 The pesticide/Aroclor compounds identified by GC/EC techniques shall be verified by an analyst competent in the interpretation of gas chromatograms and by comparison of the retention times of the suspected unknowns with the retention times of respective standards of the suspected compounds. Compounds shall also be confirmed by GC/MS techniques if the compounds are of sufficient concentration to be detected by the GC/MS.

4.2.2.5 Quantitation of Verified Compounds. The Laboratory shall quantitate components identified by GC/MS techniques by the internal standard method stipulated in Exhibit D. Where multiple internal standards are required by NYSDEC, the Laboratory shall perform quantitation utilizing the internal standards specified in Exhibit D. The Laboratory shall quantitate components analyzed by GC/EC techniques by the external standard method stipulated in Exhibit D. The Laboratory shall also perform an initial three-point calibration, verify its linearity, determine the breakdown of labile components, and determine calibration factors for all standards analyzed by GC/EC techniques as described in Exhibit D.

4.2.2.6 Tentative Identification of Non-Target Sample Components. For each analysis of a sample, the Laboratory shall conduct mass spectral library searches to determine tentative compound identifications as follows: For each volatile sample, the Laboratory shall

conduct a search to determine the possible identity of up to 30 organic compounds of greatest concentration which are not system monitoring compounds or internal standards and are not listed in Exhibit C under volatiles or semivolatiles. For each semivolatile sample, the Laboratory shall conduct a search to determine the possible identification of up to 30 organic compounds of greatest concentration, which are not surrogates or internal standards and are not listed in Exhibit C under volatiles or semivolatiles. In performing searches, the NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later), or equivalent, mass spectral library shall be used.

NOTE: *Substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion.*

4.2.2.7 Quality Assurance/Quality Control Procedures. The Laboratory shall strictly adhere to all specific QA/QC procedures prescribed in Exhibits D and E. Records documenting the use of the protocol shall be maintained in accordance with the document control procedures prescribed in Exhibit F, and shall be reported in accordance with Exhibit B and Exhibit H.

4.2.2.7.1 The Laboratory shall maintain a Quality Assurance Plan (QAP) with the objective of providing sound analytical chemical measurements. This program shall incorporate the quality control procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production.

4.2.2.7.2 Additional quality control shall be conducted in the form of the analysis of laboratory evaluation samples submitted to the Laboratory by the NYSDEC. The results of all such quality control or laboratory evaluation samples may be used as the basis for an equitable adjustment to reflect the reduced value of the data to the NYSDEC or rejection of data for: sample(s), a fraction within an SDG, or the entire SDG, and/or may be used as the basis for contract action. "Compliant performance" is defined as that which yields correct compound identification and concentration values as determined by the NYSDEC, as well as meeting the contract requirements for analysis (Exhibit D), quality assurance/quality control (Exhibit E), data reporting and other deliverables (Exhibits B and H), and sample custody, sample documentation, and standard operating procedure documentation (Exhibit F).

4.2.2.8 The Laboratory may be requested by NYSDEC to perform modified analyses. These modifications may include, but are not limited to, additional compounds, sample matrices other than soil/sediment or water, and lower quantitation limits. These requests will be made by the BWAR/PO in writing, prior to sample scheduling. If the Laboratory voluntarily elects to perform these modified analyses, these analyses will

be performed at a price agreed to by BWAR/PO. In addition, all applicable requirements specified in the Protocol will remain in effect.

4.2.3 Task III: Reporting Requirements

4.2.3.1 EPA has provided the Laboratory with formats for the reporting of data (Exhibits B and H). The Laboratory shall be responsible for completing and submitting analysis data sheets and computer-readable data on diskette (or via an alternate means of electronic transmission approved in advance by the NYSDEC) in the format specified in this Protocol and within the time specified in the Contract Performance/Delivery Schedule in Exhibit B.

4.2.3.2 Use of formats other than those designated by NYSDEC will be deemed as noncompliant. Such data are unacceptable. Resubmission in the specified format at no additional cost to the NYSDEC shall be required.

4.2.3.3 Computer-generated forms may be submitted in the hardcopy data package(s) provided that the forms are in **exact NYSDEC format**. This means that the order of data elements is the same as on each NYSDEC-required form, including form numbers and titles, page numbers, and header information.

4.2.3.4 The data reported by the Laboratory on the hardcopy data forms and the associated computer-readable data submitted by the Laboratory shall contain identical information. If discrepancies are found during government inspection, the Laboratory shall be required to resubmit either the hardcopy forms or the computer-readable data, or both sets of data, at no additional cost to the NYSDEC.

4.3 Technical and Management Capability

4.3.1 Personnel. The Laboratory shall have adequate personnel at all times during the performance of the contract to ensure that NYSDEC receives data that meet the terms and conditions of the contract and Protocol.

4.3.2 Instrumentation. The Laboratory shall have sufficient gas chromatograph/electron capture/data system (GC/EC/DS), gas chromatograph/mass spectrometer/data system (GC/MS/DS), including magnetic tape storage devices, and gel permeation chromatography system (GPC) capability to meet all the terms and conditions of the contract and Protocol.

4.3.3 Facilities. The Laboratory shall maintain a facility suitable for the receipt, storage, analysis, and delivery of the product meeting the terms and conditions of the contract and Protocol.

Section II - Specific Requirements

1.0 Introduction

The Laboratory shall receive and handle samples under the chain-of-custody and sample documentation procedures described in Exhibit F. Any discrepancies in documents or missing information is to be immediately brought to the attention of the BWAR/PO. A sample consists of all components, perhaps more than one phase, contained inside appropriate receptacles. More than one container may be used for a single sample; individual containers may contain preservatives for different analysis portions. Containers may be glass or plastic.

The Laboratory shall provide the required analytical expertise and instrumentation for analyses of the listed environmental parameters equal to or lower than the quantitation limits specified in Exhibit C. In Exhibit D, NYSDEC provides the laboratory with the specific sample preparation techniques and analytical procedures to be used along with a procedural rationale, and a schematic flow chart depicting the complete low level-medium level analytical scheme.

The Laboratory shall prepare and analyze samples within the maximum holding time specified in Exhibit I even if these times are less than the maximum 30-day completion time allowed in this Protocol.

****
* Note: The Laboratory is advised that the samples received under *
* this Protocol are often from known or suspected hazardous *
* waste sites and may contain higher (greater than 15%) levels *
* of organic and inorganic materials of a potentially hazardous *
* nature and of unknown structure and concentration and *
* should be handled throughout the analysis with appropriate *
* caution. It is the Laboratory's responsibility to take all *
* necessary measures to ensure laboratory safety. *
****

Methods for preparation of aqueous and solid samples are prescribed in Exhibit D.

For each sample received, the Laboratory may be required to perform any or all of the analyses described in Exhibit D in this Protocol. (The documentation that accompanies the sample(s) to the laboratory facility shall indicate specific analytical requirements for that sample or set of samples, by task and/or by specific target parameters.)

For the purpose of this Protocol, the analysis of a sample is defined as any, or all, of the tasks and constituents identified in Exhibits C and D, and related QA/QC as specified in Exhibit E.

***Note**: All QA/QC requirements are an inherent part of this Protocol requirement and are included in any contract bid price. The only exception being that specifically designated external QA/QC samples such as matrix duplicates, matrix spikes, matrix spike duplicates, matrix spike blanks, Laboratory Control Samples, and trip blanks are separate billable samples.*

Sample shipments to the Laboratory's facility will be scheduled and coordinated by the NYSDEC BWAR/PO.

The Laboratory shall communicate with NYSDEC authorized personnel by telephone as necessary throughout the process of sample scheduling, shipment, analysis and data reporting, to ensure that samples are properly processed. This shall include immediately notifying BWAR or the Project Officer of any irregularities with samples or sample paperwork received (noting discrepancies from verbal order placed by NYSDEC authorized personnel, problems encountered in sample analyses that will affect the data produced, and laboratory conditions that impact on timeliness of analyses and data reporting. In particular, the Laboratory shall notify BWAR in advance regarding sample data that will be late and shall specify an estimated delivery date.

Each sample received by the Laboratory should be labeled with a NYSDEC sample number, and accompanied by a Contract Lab Sample Information Sheet bearing the sample number and descriptive information regarding the sample. The Laboratory shall complete and sign the Chain-of-Custody received with the sample, recording the date of sample receipt and sample condition on receipt for each sample container. The Laboratory shall initiate an internal Chain-of-Custody for all samples submitted under this Protocol that will track the sample throughout the Laboratory. The Laboratory shall submit the signed copy of each Chain-of-Custody to BWAR with the sample data package (see contract delivery schedule). If there are problems either with the samples (e.g., mixed media, containers broken or leaking) or paperwork (e.g. Contract Lab Sample Information Sheet not with shipment; samples and sample numbers do not correspond) the Laboratory shall immediately contact BWAR for resolution.

The NYSDEC sample numbers shall be used by the Laboratory in identifying samples received under this protocol both verbally and in reports/correspondence.

The Laboratory shall accept all samples scheduled by NYSDEC provided that the total number of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Laboratory elect to accept additional samples, the Laboratory shall remain bound by all contract requirements for analysis of those samples accepted.

The following are program specific requirements:

2.0 Superfund-CLP Inorganics

Analyze Samples for Identity and Quantitation of Specific Inorganic Constituents.

2.1 For each sample received, the Laboratory may be required to perform the analyses described in paragraphs 2.2, 2.3, and 2.4 following. The documentation that accompanies the sample(s) to the laboratory facility shall indicate specific analytical requirements for that sample or set of samples.

2.2 Exhibit D, CLP, Inorganics specifies the analytical procedures that must be used. It includes instructions and references for preparation of samples containing low-to-medium concentrations of inorganics for ICP analysis; flame, graphite furnace and cold vapor AA analysis; and cyanide analysis. The identification and quantitation of analytes other than cyanide shall be accomplished using the ICP or AA methods specified in Exhibit D, CLP, Inorganics whichever method will achieve the Contract

Required Quantitation Limit (CRQL) in Exhibit C. Cyanide shall be analyzed by the individual procedures specified in Exhibit D, CLP, Inorganics.

2.3 All samples must initially be run undiluted (i.e., final product of sample preparation procedure). When an analyte concentration exceeds the calibrated or linear range, appropriate dilution and reanalysis of the prepared sample is required, as specified in Exhibit D, CLP, Inorganics.

2.4 For the purpose of this protocol, a full sample analysis is defined as analysis for any or all of the (CLP-TCL) consitituents identified in Exhibit C as specified by the Contract Lab Sample Information Sheet in accordance with the methods in Exhibit D and performance of related QA/QC as specified in Exhibit E. Duplicate sample, laboratory control sample, and spike sample analyses shall each be considered a separate full sample analysis. All other QA/QC requirements are considered an inherent part of this Protocol and are included in the contract sample unit price.

3.0 Superfund-CLP Organics

The Laboratory shall use its analytical experience and equipment to perform qualitative and quantitative analyses of the TCL organic chemical pollutants listed in Exhibit C. Preparation of the samples shall be done as described in Exhibit D, CLP, Organics. The Laboratory shall follow the protocols established by the NYSDEC for sample preparation, analysis, storage and preservation before and after the analysis (see Exhibit D, CLP, Organics).

During preparation, the Laboratory shall fortify all samples, blanks, matrix spikes, and matrix spike duplicates with surrogate spiking compounds (listed in Exhibit E). Additionally, all sample semi-volatile extracts and aliquots for volatile organics analysis shall be spiked with internal standard compounds (listed in Exhibit E) before injection or purging.

In Exhibit D, CLP, Organics, the NYSDEC provides the Laboratory with the specific analytical procedures to be used along with the definition of the specific application of these methods to this Protocol. This includes instructions for sample preparation, gas chromatographic screening, mass spectrometric identification and data evaluation. Specific ions used for searching the mass spectral data for each compound are included.

For each sample, the Laboratory shall perform the following:

3.1 Receive and Prepare Hazardous Waste Samples

3.1.1 Receive and handle samples under chain-of-custody procedures described in Exhibit F.

3.1.2 Prepare samples as described in Exhibit D. VOA analysis of water or soil samples must be completed within **10 (TEN)** days of VTSR (Validated Time of Sample Receipt). Separatory funnel extractions for pesticides in water samples must be completed within **5 (FIVE)** days of VTSR. Sonication extractions for pesticides and/or semivolatiles in soil samples must be completed within **5 (FIVE)** days of VTSR. Continuous liquid-liquid extraction for semivolatile samples

must be started within **5 (FIVE)** days, and completed within **7 (SEVEN)** days of VTSR.

Extracts of either water or soil samples must be analyzed within 40 days of extraction. This does not release the Laboratory from the contract or work plan specified data turnaround time.

3.2 Extraction and Analysis for Identification of Specific Organic Compounds.

3.2.1 Extracts and diluted aliquots prepared in paragraph 3.1. shall be analyzed by GC and GC/MS techniques given in Exhibit D, CLP, Organics for the CLP-TCL substances referenced in Exhibit C as specified by the Contract Lab Sample Information Sheet.

3.2.2 The target compounds listed in CLP-TCL, Exhibit C, shall be identified as described in the methodologies given in Exhibit D, CLP, Organics. Automated computer programs may be used to facilitate the identification.

3.3 Qualitative Verification of the Compounds Identified in Section 3.2.

3.3.1 The compounds analyzed by GC/MS techniques and initially identified in Section 3.2 shall be verified by an analyst competent in the interpretation of mass spectra by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

3.3.1.1 Elution of the sample component at the same GC relative retention time as the standard component, and

3.3.1.2 Correspondence of the sample component and standard component mass spectra.

3.3.2 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the calibration standard must be run on the same 12-hour time period as the sample.

For comparison of standard and sample component mass spectra, mass spectra obtained on the Laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes only if the Laboratory's GC/MS meets the DFTPP or BFB daily tuning requirements of Tables 1.1 and 1.2 in Exhibit E. The standard spectra used may be from a laboratory generated library or obtained from the calibration standard run used to obtain reference RRTs. The requirements for qualitative verification by comparison of mass spectra are as follows:

3.3.2.1 All ions present in the standard mass spectrum at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

3.3.2.2 The relative intensities of ions specified in 3.3.2.1 must agree within plus or minus 20 percent between the standard and sample spectra.

3.3.2.3 Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data processing programs are used to obtain the sample component spectrum, both the processed and the raw spectra must be evaluated. The verification process should favor false positives.

3.3.3 If a compound analyzed by GC/MS techniques and initially identified in Section 3.2 cannot be verified by all of the criteria in items 3.3.1 and 3.3.2 above, but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the Laboratory shall report that identification, and proceed with quantification in Section 3.4.

3.3.4 The pesticide/Aroclor compounds listed in Exhibit C and analyzed by GC techniques shall have their identifications verified by an analyst competent in the interpretation of gas chromatograms. Two criteria must be satisfied to verify the identifications:

3.3.4.1 Elution of the sample component within the retention time window (established by the procedures in Exhibit E) of the standard component analyzed on the same GC column and instrument, as specified in Exhibit D, CLP, Organics.

3.3.4.2 Analysis of the sample and standard on a second GC column with a stationary phase with retention characteristics dissimilar to that used in 3.3.4.1 above, and meeting the same criteria for elution of the sample component and the standard as in 3.3.4.1 above.

3.4 Quantification of Compounds Verified in Section 3.3.

3.4.1 The Laboratory shall quantify components analyzed by GC/MS techniques and identified in Section 3.2 and verified in Section 3.3 by the internal standard method stipulated in Exhibit D. Where multiple internal standards are required by NYSDEC, the Laboratory shall perform quantification utilizing the internal standards specified in Exhibit E, Part 2, Tables 2.1 or 2.2.

3.4.2 The Laboratory shall determine response factors for each 12-hour time period of GC/MS analysis and shall include a calibration check of the initial five-point calibration as described in Exhibit E.

3.4.3 The Laboratory shall quantify components analyzed by GC/EC techniques and identified in Section 3.2 and verified in Section 3.3 by the external standard method stipulated in Exhibit D, CLP, Organics.

3.4.4 The Laboratory shall perform an initial three-point calibration, verify its linearity, determine the breakdown of labile components, and determine calibration factors for all standards analyzed by GC/EC techniques as described in Exhibit D, CLP, Organics and Exhibit E.

3.5 Tentative Identification of Non-TCL Sample Components.

3.5.1 For each sample analyzed by GC/MS techniques, the Laboratory shall conduct mass spectral library searches to determine tentative compound identifications as follows. For each volatile fraction, the Laboratory shall conduct a search to determine the possible identity of the ten (10) organic compounds of greatest concentration which are not system monitoring compounds and are not listed in the CLP-TCL list in Exhibit C. For each semivolatile fraction, the Laboratory shall conduct a search to determine the possible identification of the (20) non-surrogate organic compounds of greatest concentration which are not listed in Exhibit C. In performing searches, the most recent release of the NIST/EPA/MSDC mass spectral library must be used.

***NOTE**: Substances with responses less than 10 percent of the nearest internal standard are not required to be searched in this fashion.*

3.5.2 Only after visual comparison of sample spectra with the spectra from the library searches will the mass spectral interpretation specialist assign a tentative identification. If the compound does not meet the identification criteria of Section 3.3, it shall be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

3.5.3 The Laboratory shall not report as tentatively identified compounds (TIC) any CLP-TCL compounds from volatile fraction (i.e., do not report late-eluting volatile compounds as TICs in the semivolatile analysis). However, The Laboratory may report pesticide target compounds that appear as semivolatile tentatively identified compounds.

3.6 Quality Assurance/Quality Control Procedures.

3.6.1 All specific quality assurance procedures prescribed in Exhibits D and E shall be strictly adhered to by the Laboratory. Records documenting the use of the Protocol shall be maintained in accordance with the document control procedures prescribed in Exhibit F, and shall be reported in accordance with Exhibit B, Reporting Requirements and Deliverables, and Exhibit H, Data Dictionary and Format for Data Deliverables in Computer-Readable Format.

3.6.2 The Laboratory shall establish a Quality Assurance Program Plan (QAPP) with the objective of providing sound analytical chemical measurements. This program shall incorporate the quality control procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production.

3.6.3 The Laboratory shall perform one spiked sample analysis (matrix spike), one duplicate spiked sample analysis (matrix spike duplicate), and one spiked blank analysis (matrix spike blank) for each group of samples of a similar matrix (for water or soil samples) and concentration level (for volatile and semivolatile soil samples only) for the following, whichever is most frequent, unless otherwise specified in a Project Workplan:

- Each Case of field samples received, OR
- Each 20 samples in a Case, OR
- Each 7 calendar day period during which field samples in a Case were received (said period beginning with the receipt of the first sample in that Sample Delivery Group).

Matrix spikes and matrix spike duplicates shall be carried through the entire analytical process from extraction to final GC/MS or GC/EC analysis, including all Protocol Performance/Delivery Requirements.

3.6.4 The Laboratory shall prepare and analyze one laboratory reagent blank (method blank) for each group of samples of a similar matrix (for water or soil samples), extracted by a similar method (separatory funnel, continuous liquid-liquid extraction, or sonication, as specified in Exhibit D), and a similar concentration level (for volatile and semivolatile soil samples only) for the following, whichever is most frequent:

- Each Case of field samples received, OR
- Each 20 samples in a Case, including matrix spikes and reanalyses, OR
- Each 7 calendar day period during which field samples in a Case were received (said period beginning with the receipt of the first sample in that Sample Delivery Group), OR
- Whenever samples are extracted.

Volatile analysis requires one method blank for each 12-hour time period when volatile target compounds are analyzed.

Semivolatile and pesticide method blanks shall be carried through the entire analytical process from extraction to final GC/MS or GC/EC analysis, including all Protocol Performance/Delivery Requirements.

3.6.5 The Laboratory shall verify instrument performance for each 12-hour time period, to include the following: Decafluorotriphenylphosphine (DFTPP) and/or Bromofluorobenzene (BFB) as applicable, and a specific calibration using standards of defined concentration to monitor response, retention time, and mass spectra.

3.6.6 Additional quality control shall be conducted in the form of the analysis of laboratory evaluation samples submitted to the Laboratory by the NYSDEC. The results of all such control or laboratory evaluation samples may be used as grounds for termination of noncompliant Laboratories. "Compliant performance" is defined as that which yields correct compound identification and concentration values as determined by the NYSDEC, as well as meeting the contract requirements for analysis (Exhibit D), quality assurance/quality control (Exhibit E), data reporting and other deliverables (Exhibits B and H), and sample custody, sample documentation and SOP documentation (Exhibit F).

4.0 40 CFR Inorganics and Conventionals (Part 136)

4.1 In Exhibit D, 100, 200, 300, and 400 Series, NYSDEC provides the Laboratory with specific analytical procedures that may be used. Specific regulatory requirements that may limit the usage of these methods are provided in Section IV of this Exhibit A. These methods include instructions and references for sample preparation of samples containing low-to-medium concentrations of inorganics and organics for ICP analysis, flame, flameless and cold vapor AA analysis and classical wet-chemical analysis. The identification and quantification of elements shall be accomplished using either ICP or AA methods for metals whichever method will achieve the contract required quantitation limit (Exhibit C). Conventionals shall be analyzed by the individual procedures specified in Exhibit D.

4.2 The Laboratory shall establish and use on a continuing basis QA/QC procedures including the daily or (as required) more frequent use of standard reference solutions from USEPA or the National Institute of Standards and Technology (NIST), or secondary standards traceable thereto, where available at appropriate concentrations, i.e., standard solutions designed to insure that operating parameters of equipment and procedures, from sample collection through identification and quantification, produce reliable data. Exhibit E specifies the QA/QC procedures required. Additional quality assurance and quality control may be required on a semi-annual basis in the form of Performance Evaluation Samples submitted by NYSDEC for analysis and instrument verifications. (See Exhibit E)

4.3 For the purpose of this Protocol one analysis unit by ICP spectroscopy, flame, flameless, cold vapor AA and conventionals shall be considered the analysis of the appropriate blank samples, check samples and standards (with the frequency specified in Exhibit E) and the sample for one or more parameters listed in Exhibit C as specified by the Contract Lab Sample Information Sheet. A full sample analysis shall be considered one or more of the analysis units defined above. Duplicate sample, laboratory control sample, and matrix spiked sample analyses shall each be considered a separate and billable sample analysis.

4.4 Definition of a Sample - A sample consists of all components, perhaps more than one phase, contained inside appropriate receptacles. More than one container may be used for a single sample; individual containers may contain preservatives for different analysis portions. Containers may be glass or plastic.

4.5 The Laboratory shall adhere to chain-of-custody and document control procedures described in Exhibit G. Documentation as described therein shall be required to show that all procedures are being strictly followed. This documentation must be reported for each sample as specified in Exhibit B. The data must be reported in the exact format of the NYSDEC forms, specified in Exhibit B.

4.6 The Laboratory must designate and utilize key personnel meeting the minimum requirements, as specified in Section III of this Exhibit, and comply with all terms and conditions of the contract. NYSDEC reserves the right to review personnel qualifications and reject those not meeting the minimum experience requirements. Experience is defined as more than 50 percent of the personnel's productive work time in active participation of a given task.

5.0 40 CFR Inorganics and Conventionals (Parts 261, 264, 268, 270)

5.1 In Exhibit D, SW846, NYSDEC provides the Laboratory with specific analytical procedures to be used. Specific regulatory requirements that may limit the usage of these methods are provided in Section IV of this Exhibit A. These methods include instructions and references for sample preparation of samples containing low-to-medium concentrations of inorganics and organics for ICP analysis, flame, flameless and cold vapor AA analysis and classical wet-chemical analysis. The identification and quantification of elements shall be accomplished using either ICP or AA methods for metals whichever method will achieve the contract required quantitation limit (Exhibit C). Conventionals shall be analyzed by the individual procedures specified in Exhibit D.

5.2 The Laboratory shall establish and use on a continuing basis QA/QC procedures including the daily or (as required) more frequent use of standard reference solutions from USEPA or the National Bureau of Standards, or secondary standards traceable thereto, where available at appropriate concentrations, i.e., standard solutions designed to insure that operating parameters of equipment and procedures, from sample collection through identification and quantification, produce reliable data. Exhibit E specifies the QA/QC procedures required. Additional quality assurance and quality control may be required on a semi-annual basis in the form of Performance Evaluation Samples submitted by NYSDEC for analysis and instrument verifications. (See Exhibit E)

5.3 For the purpose of this protocol one analysis unit by ICP spectroscopy, flame, flameless, cold vapor AA and conventionals shall be considered the analysis of the appropriate blank samples, check samples and standards (with the frequency specified in Exhibit E) and the sample for one or more parameters listed in Exhibit C as specified by the Contract Lab Sample Information Sheet. A full sample analysis shall be considered one or more of the analysis units defined above. Duplicate sample, laboratory control sample, and matrix spiked sample analyses shall each be considered a separate and billable sample analysis.

5.4 Definition of a Sample - A sample consists of all components, perhaps more than one phase, contained inside appropriate receptacles. More than one container may be used for a single sample; individual containers may contain preservatives for different analysis portions. Containers may be glass or plastic.

5.5 The Laboratory shall adhere to chain-of-custody and document control procedures described in Exhibit G. Documentation as described therein shall be required to show that all procedures are being strictly followed. This documentation must be reported for each sample as specified in Exhibit B. The data must be reported in the exact format of the NYSDEC forms, specified in Exhibit B.

5.6 The Laboratory must designate and utilize key personnel meeting the minimum requirements, as specified in Section III of this Exhibit, and comply with all terms and conditions of the contract. NYSDEC reserves the right to review personnel qualifications and reject those not meeting the minimum experience requirements. Experience is defined as more than 50 percent of the personnel's productive work time in active participation of a given task.

6.0 40CFR Organics (Part 136)

The Laboratory shall use its analytical experience and equipment to perform qualitative and quantitative analyses of the organic chemical pollutants listed in Exhibit C. Preparation of the samples shall be done as described in Exhibit D, 600 and 1600 Series. The Laboratory shall follow the protocols established by the NYSDEC for sample preparation, analysis, storage and preservation, before and after the analysis (see Exhibit D).

During preparation, the Laboratory shall fortify all standards, samples, blanks, matrix spikes, and matrix spike duplicates with surrogate spiking compounds (listed in Exhibit E). Additionally, all sample semivolatile extracts and aliquots for volatile organics analysis shall be spiked with internal standard compounds (listed in Exhibit E) before injection or purging.

In Exhibit D, 600 and 1600 Series, NYSDEC provides the Laboratory with the specific analytical procedures to be used. Specific regulatory requirements that may limit the usage of these methods are provided in Section IV of this Exhibit A. These methods include instructions for sample preparation, gas chromatographic, thin layer chromatographic and high performance liquid chromatographic analysis, mass spectrometric identification and data evaluation. Specific ions used for searching the mass spectral data for each compound are included.

For each sample, the Laboratory shall perform the following:

6.1 Receive and Prepare Organic Samples.

6.1.1 Receive and handle samples under the chain-of-custody procedures described in Exhibit G.

6.1.2 Prepare samples as described in Exhibit D. VOA analyses shall be performed within **10 (TEN)** days of sample receipt. Sample extractions shall be started within **5 (FIVE)** days, and completed within **7 (SEVEN)** days of sample receipt. Sample extracts must be completely analyzed within 40 days of extraction. (**NOTE**: This does not preclude the Protocol requirement of a 30-day turnaround of analytical data.)

6.2 Extraction and Analysis for Identification of Specific Organic Compounds.

6.2.1 Extracts and diluted aliquots prepared in Section 6.1. shall be analyzed by GC and GC/MS techniques given in Exhibit D for the 40CFR organic substances referenced in Exhibit C as specified in the Contract Lab Sample Information Sheet.

6.2.2 The target compounds listed in Exhibit C, 40 CFR shall be identified as described in the methodologies given in Exhibit D. Automated computer programs may be used to facilitate the identification.

6.3 Qualitative Verification of the Compounds Identified in Section 6.2.

6.3.1 The compounds initially identified by GC/MS using methods 624, 625, 1624, or 1625 in Section 6.2 shall be verified by an analyst competent in the

interpretation of mass spectra by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra. This procedure requires the use of multiple internal standards.

6.3.2 The compounds initially identified by GC or HPLC procedures in Section 6.2 shall be verified by an analyst competent in the interpretation of chromatograms generated by the method performed, by comparison of the sample chromatogram to the chromatogram of a standard of the suspected compound. GC verification must be accomplished by the elution of the sample component at the same GC relative retention time as the standard component on two dissimilar GC columns. The Laboratory may confirm analytes by GC/MS, however, verification of comparable MDLs must be provided in the data package.

6.3.3 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the calibration standard must be run on the same 12-hour time period as the sample.

For comparison of standard and sample component mass spectra, mass spectra obtained on the Laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes only if the Laboratory's GC/MS meets the DFTPP and BFB daily tuning requirements of Tables 1.1 and 1.2 in Exhibit E. The standard spectra used may be from a laboratory generated library or obtained from the calibration standard run used to obtain reference RRTs.

These requirements for qualitative verification by comparison of mass spectra are as follows:

6.3.3.1 All ions present in the standard mass spectrum at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

6.3.3.2 The relative intensities of ions specified in (1) must agree within plus or minus 20 percent between the standard and sample spectra.

6.3.3.3 Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data processing programs are used to obtain the sample component spectrum, both the processed and the raw spectra must be evaluated. In Section 6.3, the verification process should favor false positives.

6.4 Quantification of Compounds Verified in Section 6.3.

6.4.1 The Laboratory shall quantify components identified in Section 6.2 and verified in Section 6.3 by the internal standard method stipulated in Exhibit D. Where multiple internal standards are required by NYSDEC, the Laboratory shall

perform quantitation utilizing the internal standards specified in Exhibit E, Part 2, Tables 2.1 or 2.2.

6.4.2 The Laboratory shall determine response factors for each 12-hour time period and shall include a calibration check of the initial five point calibration as described in Exhibit E.

6.5 Tentative Identification of Non-TCL Sample Components.

6.5.1 For each sample analyzed by GC/MS, the Laboratory shall execute library searches on substances not listed in the 40CFR Organics list in Exhibit C. A maximum of 10 substances of greatest apparent concentration not listed in the 40CFR organics list in Exhibit C for each volatile organic fraction, and a maximum of 20 substances of greatest apparent concentration not listed in Exhibit C for the combined base/ neutral/acid fraction shall be tentatively identified via a forward search of the most recent available NIST/EPA/MSDC mass spectral library. (Substances with responses less than 10 percent of the nearest internal standard are not required to be searched in this fashion.) Only after visual comparison of sample spectra with the spectra from the library searches will the mass spectral interpretation specialist assign a tentative identification. If the unknown does not meet the identification criteria of Section 6.3 it should be reported as unknown.

7.0 40CFR Organics (Parts 261, 264, 268, 270)

The Laboratory shall use its analytical experience and equipment to perform qualitative and quantitative analyses of the organic chemical pollutants listed in Exhibit C. Preparation of the samples shall be done as described in Exhibit D, SW846. The Laboratory shall follow the protocols established by the NYSDEC for sample preparation, analysis, storage and preservation before and after the analysis (see Exhibit D).

During preparation, the Laboratory shall fortify all standards, samples, blanks, matrix spikes, and matrix spike duplicates with surrogate spiking compounds (listed in Exhibit E). Additionally, all sample semivolatile extracts and aliquots for volatile organics analysis shall be spiked with internal standard compounds (listed in Exhibit E) before injection or purging.

In Exhibit D, SW846, the NYSDEC provides the Laboratory with the specific analytical procedures to be used. Specific regulatory requirements that may limit the usage of these methods are provided in Section IV of this Exhibit A. These methods include instructions for sample preparation, gas chromatographic, thin layer chromatographic and high performance liquid chromatographic analysis, mass spectrometric identification and data evaluation. Specific ions used for searching the mass spectral data for each compound are included.

For each sample, the Laboratory shall perform the following:

7.1 Receive and Prepare Organic Samples.

7.1.1 Receive and handle samples under the chain-of-custody procedures described in Exhibit G.

7.1.2 Prepare samples as described in Exhibit D. VOA analyses shall be performed within **10 (TEN)** days of sample receipt, regardless of sample matrix. Sample extractions shall be started within **5 (FIVE)** days, and completed within **7 (SEVEN)** days of sample receipt, regardless of sample matrix. Sample extracts must be completely analyzed within 40 days of extraction. (**NOTE**: This does not preclude the Protocol requirement of a 30-day turnaround of analytical data.)

7.2 Extraction and Analysis for Identification of Specific Organic Compounds.

7.2.1 Extracts and diluted aliquots prepared in Section 7.1. shall be analyzed by GC and GC/MS techniques given in Exhibit D for the 40 CFR organic substances referenced in Exhibit C as specified in the Contract Lab Sample Information Sheet.

7.2.2 The target compounds listed in Exhibit C, 40 CFR shall be identified as described in the methodologies given in Exhibit D. Automated computer programs may be used to facilitate the identification.

7.3 Qualitative Verification of the Compounds Identified in Section 7.2.

7.3.1 The compounds initially identified by GC/MS using methods 8240, 8260, 8250, or 8270 in Section 7.2 shall be verified by an analyst competent in the interpretation of mass spectra by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra. This procedure requires the use of multiple internal standards.

7.3.2 The compounds initially identified by GC or HPLC procedures in Section 7.2 shall be verified by an analyst competent in the interpretation of chromatograms generated by the method performed, by comparison of the sample chromatogram to the chromatogram of a standard of the suspected compound. GC verification must be accomplished by the elution of the sample component at the same GC relative retention time as the standard component on two dissimilar GC columns. The Laboratory may confirm analytes by GC/MS, however, verification of comparable MDLs must be provided in the data package.

7.3.3 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the calibration standard must be run on the same 12-hour time period as the sample.

For comparison of standard and sample component mass spectra, mass spectra obtained on the Laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes only if the Laboratory's GC/MS meets the DFTPP and BFB daily tuning requirements of Tables 1.1 and 1.2 in Exhibit E. The standard spectra used may be from a laboratory-generated library or obtained from the calibration standard run used to obtain reference RRTs.

These requirements for qualitative verification by comparison of mass spectra are as follows:

7.3.3.1 All ions present in the standard mass spectrum at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

7.3.3.2 The relative intensities of ions specified in (1) must agree within plus or minus 20 percent between the standard and sample spectra.

7.3.3.3 Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data processing programs are used to obtain the sample component spectrum, both the processed and the raw spectra must be evaluated. In Section 7.3, the verification process should favor false positives.

7.4 Quantification of Compounds Verified in Section 7.3.

7.4.1 The Laboratory shall quantify components identified in Section 7.2 and verified in Section 7.3 by the internal standard method stipulated in Exhibit D. Where multiple internal standards are required by NYSDEC, the Laboratory shall perform quantitation utilizing the internal standards specified in Exhibit E.

7.4.2 The Laboratory shall determine response factors for each 12-hour time period and shall include a calibration check of the initial five point calibration as described in Exhibit E.

7.5 Tentative Identification of Non-TCL Sample Components.

7.5.1 For each sample analyzed by GC/MS, the Laboratory shall execute library searches on substances not listed in the 40CFR Organics list in Exhibit C. A maximum of 10 substances of greatest apparent concentration not listed in the 40CFR organics list in Exhibit C for each volatile organic fraction, and a maximum of 20 substances of greatest apparent concentration not listed in Exhibit C for the combined base/ neutral/acid fraction shall be tentatively identified via a forward search of the most recent available NIST/EPA/MSDC mass spectral library. (Substances with responses less than 10 percent of the nearest internal standard are not required to be searched in this fashion.) Only after visual comparison of sample spectra with the spectra from the library searches will the mass spectral interpretation specialist assign a tentative identification. If the unknown does not meet the identification criteria of Section 7.3 it should be reported as unknown.

8.0 Organics (500 Series)

The Laboratory shall use its analytical experience and equipment to perform qualitative and quantitative analyses of the organic chemical pollutants listed in Exhibit C. Preparation of the samples shall be done as described in Exhibit D, 500 Series. The Laboratory shall follow the protocols established by the NYSDEC for sample preparation, analysis, reporting and deliverables, storage and preservation before and after the analysis (see Exhibit D).

During preparation, the Laboratory shall fortify all samples, standards, blanks, matrix spikes, and matrix spike duplicates with surrogate spiking compounds (listed in Exhibit E). Additionally, all sample semi-volatile extracts and aliquots for volatile organics analysis shall be spiked with internal standard compounds (listed in Exhibit E) before injection or purging.

In Exhibit D, 500 Series, the NYSDEC provides the Laboratory with the specific analytical procedures to be used. These methods include instructions for sample preparation, gas chromatographic, thin layer chromatographic and high performance liquid chromatographic analysis, mass spectrometric identification and data evaluation. Specific ions used for searching the mass spectral data for each compound are included.

For each sample, the Laboratory shall perform the following:

8.1 Receive and Prepare Organic Samples.

8.1.1 Receive and handle samples under the chain-of-custody procedures described in Exhibit G.

8.1.2 Prepare samples as described in Exhibit D. VOA analyses shall be performed within **10 (TEN)** days of sample receipt. Semivolatile extractions shall be started within **5 (FIVE)** days, and completed within **7 (SEVEN)** days of sample receipt. Sample extracts must be completely analyzed within 40 days of extraction. (**NOTE**: This does not preclude the Protocol requirement of a 30-day turnaround of analytical data.)

8.2 Extraction and Analysis for Identification of Specific Organic Compounds.

8.2.1 Extracts and diluted aliquots prepared in Section 8.1. shall be analyzed by GC and GC/MS techniques given in Exhibit D for the 40 CFR organic substances referenced in Exhibit C as specified in the Contract Lab Sample Information Sheet.

8.2.2 The target compounds listed in Exhibit C, 40 CFR shall be identified as described in the methodologies given in Exhibit D. Automated computer programs may be used to facilitate the identification.

8.3 Qualitative Verification of the Compounds Identified in Section 8.2.

8.3.1 The compounds initially identified by GC/MS in Section 8.2 shall be verified by an analyst competent in the interpretation of mass spectra by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra. This procedure requires the use of multiple internal standards.

8.3.2 The compounds initially identified by GC or HPLC procedures in Section 8.2 shall be verified by an analyst competent in the interpretation of chromatograms generated by the method performed, by comparison of the sample

chromatogram to the chromatogram of a standard of the suspected compound. GC verification must be accomplished by the elution of the sample component at the same GC relative retention time as the standard component on two dissimilar GC columns. The Laboratory may confirm analytes by GC/MS, however, verification of comparable MDLs must be provided in the data package.

8.3.3 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the previous standard. The calibration standard must be run as indicated in the appropriate method.

For comparison of standard and sample component mass spectra, mass spectra obtained on the Laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes only if the Laboratory's GC/MS meets the DFTPP and BFB daily tuning requirements of Tables 1.1 and 1.2 in Exhibit E. The standard spectra used may be from a laboratory generated library or obtained from the calibration standard run used to obtain reference RRTs.

These requirements for qualitative verification by comparison of mass spectra are as follows:

8.3.3.1 All ions present in the standard mass spectrum at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

8.3.3.2 The relative intensities of ions specified in (1) must agree within plus or minus 20 percent between the standard and sample spectra.

8.3.3.3 Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data processing programs are used to obtain the sample component spectrum, both the processed and the raw spectra must be evaluated. In Section 8.3, the verification process should favor false positives.

8.4 Quantification of Compounds Verified in Section 8.3.

8.4.1 The Laboratory shall quantify components identified in Section 8.2 and verified in Section 8.3 by the internal standard method stipulated in Exhibit D. Where multiple internal standards are required by NYSDEC, the Laboratory shall perform quantitation utilizing the internal standards specified in Exhibit E, Part 2, Tables 2.1 or 2.2.

8.4.2 The Laboratory shall determine response factors at the method specified frequency and shall include a calibration check of the initial five point calibration as described in Exhibit E.

8.5 Tentative Identification of Non-TCL Sample Components.

8.5.1 For each sample analyzed by GC/MS, the Laboratory shall execute library searches on substances not listed in the 40 CFR Organics list in

Exhibit C. A maximum of 10 substances of greatest apparent concentration not listed in the 40 CFR organics list in Exhibit C for each volatile organic fraction, and a maximum of 20 substances of greatest apparent concentration not listed in Exhibit C for the combined base/ neutral/acid fraction shall be tentatively identified via a forward search of the most recent available NIST/EPA/MSDC mass spectral library. (Substances with responses less than 10 percent of the nearest internal standard are not required to be searched in this fashion.) Only after visual comparison of sample spectra with the spectra from the library searches will the mass spectral interpretation specialist assign a tentative identification. If the unknown does not meet the identification criteria of Section 8.3 it should be reported as unknown.

9.0 Non-Conventional Pesticides

The Laboratory shall use its analytical experience and equipment to perform qualitative and quantitative analyses of the organic chemical pollutants listed in Exhibit C. Preparation of the samples shall be done as described in Exhibit D, 600 and 1600 Series. The Laboratory shall follow the protocols established by the NYSDEC for sample preparation, analysis, storage and preservation before and after the analysis (see Exhibit D).

During preparation, the Laboratory shall fortify all samples, standards, blanks, matrix spikes, and matrix spike duplicates with surrogate spiking compounds (listed in Exhibit E). Additionally, all sample semi-volatile extracts and aliquots for volatile organics analysis shall be spiked with internal standard compounds (listed in Exhibit E) before injection or purging.

In Exhibit D, 600 and 1600, the NYSDEC provides the Laboratory with the specific analytical procedures to be used. Specific regulatory requirements that may limit the usage of these methods are provided in Section IV of this Exhibit A. These methods include instructions for sample preparation, gas chromatographic, thin layer chromatographic and high performance liquid chromatographic analysis, mass spectrometric identification and data evaluation. Specific ions used for searching the mass spectral data for each compound are included.

For each sample, the Laboratory shall perform the following:

9.1 Receive and Prepare Organic Samples.

9.1.1 Receive and handle samples under the chain-of-custody procedures described in Exhibit G.

9.1.2 Prepare samples as described in Exhibit D. Sample extractions shall be started within **5 (FIVE)** days and completed within **7 (SEVEN)** days of sample receipt. Sample extracts must be completely analyzed within 40 days of extraction. (**NOTE**: This does not preclude the protocol requirement of a 30-day turnaround of analytical data.)

9.2 Extraction and Analysis for Identification of Specific Organic Compounds.

9.2.1 Extracts and diluted aliquots prepared in Section 9.1. shall be analyzed by GC and GC/MS techniques given in Exhibit D for the 40 CFR organic

substances referenced in Exhibit C as specified in the Contract Lab Sample Information Sheet.

9.2.2 The target compounds listed in Exhibit C, shall be identified as described in the methodologies given in Exhibit D. Automated computer programs may be used to facilitate the identification.

9.3 Qualitative Verification of the Compounds Identified in Section 9.2.

9.3.1 The compounds initially identified by GC/MS in Section 9.2 shall be verified by an analyst competent in the interpretation of mass spectra by comparison of the suspect mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra. This procedure requires the use of multiple internal standards.

9.3.2 The compounds initially identified by GC or HPLC procedures in Section 9.2 shall be verified by an analyst competent in the interpretation of chromatograms generated by the method performed, by comparison of the sample chromatogram to the chromatogram of a standard of the suspected compound. GC verification must be accomplished by the elution of the sample component at the same GC relative retention time as the standard component on two dissimilar GC columns. The Laboratory may confirm analytes by GC/MS, however, verification of comparable MDLs must be provided in the data package.

9.3.3 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the calibration standard must be run at the frequency specified in the method.

For comparison of standard and sample component mass spectra, mass spectra obtained on the Laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes only if the Laboratory's GC/MS meets the DFTPP and BFB daily tuning requirements of Tables 1.1 and 1.2 in Exhibit E. The standard spectra used may be from a laboratory generated library or obtained from the calibration standard run used to obtain reference RRTs.

These requirements for qualitative verification by comparison of mass spectra are as follows:

9.3.3.1 All ions present in the standard mass spectrum at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

9.3.3.2 The relative intensities of ions specified in (1) must agree within plus or minus 20 percent between the standard and sample spectra.

9.3.3.3 Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and

accounted for by the analyst making the comparison. When GC/MS computer data processing programs are used to obtain the sample component spectrum, both the processed and the raw spectra must be evaluated. In Section 9.3, the verification process should favor false positives.

9.4 Quantification of Compounds Verified in Section 9.3.

9.4.1 The Laboratory shall quantify components identified in Section 9.2 and verified in Section 9.3 by the internal standard method stipulated in Exhibit D. Where multiple internal standards are required by NYSDEC, the Laboratory shall perform quantitation utilizing the internal standards specified in Exhibit E, Part 2, Tables 2.1 or 2.2.

9.4.2 The Laboratory shall determine response factors at the method specified frequency and shall include a calibration check of the initial five point calibration as described in Exhibit E.

9.5 Tentative Identification of Non-TCL Sample Components.

9.5.1 For each sample analyzed by GC/MS, the Laboratory shall execute library searches on substances not listed in the 40 CFR Organics list in Exhibit C. A maximum of 10 substances of greatest apparent concentration not listed in the 40 CFR organics list in Exhibit C for each volatile organic fraction, and a maximum of 20 substances of greatest apparent concentration not listed in Exhibit C for the combined base/ neutral/acid fraction shall be tentatively identified via a forward search of the most recent available NIST/EPA/MSDC mass spectral library. (Substances with responses less than 10 percent of the nearest internal standard are not required to be searched in this fashion.) Only after visual comparison of sample spectra with the spectra from the library searches will the mass spectral interpretation specialist assign a tentative identification. If the unknown does not meet the identification criteria of Section 9.3 it should be reported as unknown.

10.0 Quality Assurance/Quality Control Procedures

10.1 All specific quality assurance procedures prescribed (Exhibit E, QA/QC Requirements) shall be strictly adhered to by the Laboratory. Records documenting the use of the protocol shall be maintained in accordance with the document control procedures prescribed in Exhibit F, and reported in accordance with Exhibit B, "Reporting Requirements and Deliverables".

10.2 The Laboratory shall establish and use on a continuing basis QA/QC procedures including the daily or (as required) more frequent use of standard reference solutions from USEPA, the National Institute of Standards and Technology or secondary standards traceable thereto, where available at appropriate concentrations (i.e., standard solutions designed to ensure that operating parameters of equipment and procedures, from sample collection through identification and quantitation, produce reliable data). Exhibit E specifies the QA/QC procedures required.

10.3 The Laboratory shall perform one spiked sample analysis (matrix spike), one duplicate/spiked duplicate sample analysis (matrix duplicate/matrix spike duplicate),

and one matrix spike blank for each group of samples of a similar matrix (for water or soil samples) and concentration level (for soil samples only), once:

- each Sample Delivery Group (SDG) of field samples received, OR
- each 20 field samples in an SDG, OR
- each 7 calendar day period during which field samples in a SDG were received (said period beginning with the receipt of the first sample in that SDG),

OR AS DIRECTED BY THE BUREAU OF WATERSHED ASSESSMENT AND RESEARCH OR THE PROJECT OFFICER.

whichever is most frequent.

Specific samples to be spiked will be identified to the Laboratory by either BWAR or the Project Officer. Matrix spikes, matrix spike duplicates or matrix spike blank as required by the method shall be carried through the entire analytical process from extraction to final GC/MS or GC/EC analysis, including all Contract Performance/ Delivery Requirements (see Exhibit B and E).

10.4 The Laboratory shall prepare and analyze one laboratory reagent blank (method blank) for each group of samples of a similar matrix (for water or soil samples), extracted by a similar method (separatory funnel or continuous liquid-liquid extraction), and a similar concentration level (for soil samples only), once:

- each SDG of field samples received, OR
- each 20 field samples in a SDG, OR
- each 7 calendar day period during which field samples in a SDG were received (said period beginning with the receipt of the first sample in that SDG), OR
- whenever samples are extracted,

whichever is most frequent.

Volatile analysis requires one method blank for each 12-hour time period when volatile TCL compounds are analyzed.

Semivolatile and pesticide method blanks shall be carried through the entire analytical process from extraction to final GC/MS or GC/EC analysis, including all Contract Performance/Delivery Requirements (see Contract Schedule).

10.5 The Laboratory shall perform instrument calibration (by "hardware tune") at each method specified frequency, to include: decafluorotriphenyl-phosphine (DFTPP) and/or bromofluorobenzene (BFB) as applicable, and a specific calibration using standards of defined concentration to monitor response, retention time and mass spectra.

Additional quality control shall be conducted in the form of the analysis of Performance Evaluation check samples submitted to the Laboratory as authorized by NYSDEC. The results of comparison studies are due within 30 calendar days of receipt of the samples.

The results of all such control or PE check samples may be used as grounds for termination of noncompliant laboratories. "Compliant performance" is defined as that which yields correct compound identification and concentration values as determined by NYSDEC, as well as meeting the contract requirements for analysis (Exhibits C and D), quality assurance/quality control (Exhibit E), data reporting and other deliverables (Exhibits B and H), and sample custody, sample documentation and SOP documentation (Exhibit F).

10.6 After award of a contract and before the first sample results are due and on a semiannual basis thereafter, using standard reference materials, the Laboratory shall determine the analytical instrument detection limits (IDLs). The Laboratory should compare these instrumental detection limits with sample detection limits to determine if in-house quality control procedures are effective.

For inorganics the IDL is determined by multiplying by the Students t-Test value the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water) at a concentration of 3x-5x the estimated IDL on three days with a minimum of seven measurements per day.

For organics the IDL is determined by multiplying by the Students t-Test value the standard deviation obtained for minimum of three replicate analyses of a standard solution at a concentration of 3x-5x the estimated IDL (each analyte in reagent water).

These analyses shall be performed using the instrumental conditions in Exhibit D on standards in solvent for base/neutrals, acids, and pesticides/PCBs and on standards diluted into reagent water for volatile organics and inorganics. The standard deviation (s_c) at this concentration is then calculated with n-1 degrees of freedom. The instrument detection limits shall be calculated as follows:

$$IDL = t_{n-1} \times s_c$$

where t_{n-1} is the Students t-Test value for a 99% confidence level at the n-1 level and n is the number of replicates. For three replicates, $t_{n-1} = 6.965$ and for twenty-one replicates, $t_{n-1} = 2.528$.

These values shall be supplied to the data users (see Exhibit B, "Reporting Requirements and Deliverables").

11.0 Reporting Requirements

NYSDEC has provided to the Laboratory formats for the reporting of data (Exhibits B and H). The Laboratory shall be responsible for completing and returning weekly reports, analysis data sheets and submitting computer-readable data on floppy diskette in the format specified in this Protocol and within the time specified in the Contract Performance/Delivery Schedule.

11.1 Use of formats other than those designated by NYSDEC will be deemed as noncompliance. Such data are unacceptable. Resubmission in the specified format at no additional cost to the government will be required. In addition the Laboratory may be subject to late reporting penalties.

11.2 Computer generated forms may be submitted in the hardcopy data package(s) provided that the forms are in EXACT NYSDEC FORMAT. This means that

the order of data elements is the same as on each NYSDEC required form, including form numbers and titles, page numbers and header information.

11.3 The data reported by the Laboratory on the hardcopy data forms and the associated computer-readable data submitted by the Laboratory must contain identical information. If during government inspection discrepancies are found, the Laboratory shall be required to resubmit either or both sets of data at no additional cost to the government within 10 days of the date of a written request to do so. All requests regarding clarifications, omissions, or transcription errors must be adequately addressed within the 10-day time period.

12.0 Laboratory Equipment Requirements

The Laboratory shall provide analytical equipment and technical expertise for this Protocol as specified below: The Laboratory shall maintain, at a minimum, all analytical equipment allocated for a contract or work plan under this Protocol.

12.1 Inductively coupled plasma (ICP) emission spectrometer with the capability to analyze metals sequentially or simultaneously and/or atomic absorption spectrometer (AA) equipped for flame analysis.

12.2 Atomic absorption (AA) spectrometer equipped with graphite furnace.

12.3 Atomic absorption spectrometer equipped for cold vapor AA (or a specific mercury analyzer) analysis capabilities.

12.4 Analytical equipment/apparatus for classical wet chemical analyses as described in Exhibit D.

12.5 Gas chromatograph(s) equipped with a purge and trap device and electrolytic conductivity and photoionization detectors for volatile organic analysis.

12.6 The Laboratory shall have sufficient gas chromatographs equipped with electron capture detectors and data systems to meet the pesticide/PCB analysis required by a contract or project work plan. The GC/EC/DS for Superfund-CLP pesticide analysis shall be equipped with wide bore capillary columns and a suitable detector and data system as described in Exhibit D, CLP, Organics.

12.7 The GC analyses performed under this protocol shall be performed using method specified columns and shall be equipped with detectors specified for those individual analyses as described in Exhibit D.

12.8 Gas chromatograph/mass spectrometer/data system (GC/ MS/DS) equipped with a purge and trap device for volatile organic analysis. A separate, dedicated instrument is required for the analysis of low concentration volatile organics by Methods 525.2 and Exhibit D, CLP, Organics.

The Laboratory's GC/MS instrument system for volatiles shall have the following:

12.8.1 The GC/MS shall be equipped with a glass jet separator when using packed columns.

12.8.2 The computer shall be interfaced by hardware to the mass spectrometer and be capable of acquiring continuous mass scans for the duration of the chromatographic program.

12.8.3 The computer shall be equipped with mass storage devices for saving all data from the GC/MS runs.

12.8.4 Computer software shall be available to allow searching GC/MS runs for specific ions and plotting the intensity of the ions with respect to time or scan number.

12.8.5 A computer data system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA/MSDC mass spectral library shall be used as the reference library. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

12.9 Gas chromatograph/mass spectrometer/data system (GC/MS/DS) for semi-volatile organic analysis.

The Laboratory's GC/MS instrument system for semi-volatiles shall have the following:

12.9.1 The computer shall be interfaced by hardware to the mass spectrometer and be capable of acquiring continuous mass scans for the duration of the chromatographic program.

12.9.2 The computer shall be equipped with mass storage devices for saving all data from the GC/MS runs.

12.9.3 Computer software shall be available to allow searching GC/MS runs for specific ions and plotting the intensity of the ions with respect to time or scan number.

12.9.4 The GC/MS shall be equipped with a split/splitless injector and GC to MS interface capable of extending a fused silica capillary column into the ion source. The column is to be 30 meters long by 0.25 or 0.32 mm inside diameter, bonded DB-5, fused silica or equivalent.

12.9.5 A computer data system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an

Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA/MSDC mass spectral library shall be used as the reference library. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

12.10 The Laboratory shall provide adequate instrument redundancy, through multiple instruments and/or extensive in-house stocks of replacement parts and circuit boards, to ensure that at least one operating instrument of each type necessary may reasonably be expected to be available at any one time. The Laboratory shall maintain, at the minimum, all analytical equipment allocated for this Protocol at the time of the on-site audit.

12.11 The Laboratory shall use a magnetic tape storage device capable of recording data suitable for long-term off-line storage. The Laboratory shall retain all raw GC/MS data acquired during the entire contract or project period on magnetic tape in appropriate instrument manufacturer format. The Laboratory is required to retain these tapes, with associated hardcopy tape logbook identifying tape contents (see Exhibit E) for a period of three (3) years from the end of the contract or project. The Laboratory shall provide the magnetic tapes to the NYSDEC within seven (7) days of request by the BWAR or the Project Officer.

12.12 The Laboratory shall have a computerized MS library search system capable of providing a forward comparison, utilizing the standard spectra contained in the mass spectral library. The most recent release of the NIST/EPA/MSDC mass spectral library must be used.

12.12.1 The system shall provide a numerical ranking of the standard spectra most closely corresponding to the sample spectra examined.

12.12.2 The data system shall remove background signals from suspect chemical pollutant spectra.

12.13 The Laboratory shall have in-house (at the laboratory facility) and operable, a device capable of analyzing purgeable organics as described in Exhibit D.

12.14 The Laboratory shall have, in-house, the appropriate standards for <u>all</u> target compounds listed in Exhibit C, which are specified in a contract or project work plan, prior to accepting any samples under this Protocol.

12.15 The Laboratory shall have an IBM or IBM-compatible minicomputer or PC capable of recording required sample data on 1.44 M-Byte 3.5 inch diskettes, in ASCII text file format and in accordance with the file, record and field specifications listed in Exhibit H.

13.0 Laboratory Personnel

The minimum functional requirements necessary to meet the terms and conditions of this Protocol are listed in items 13.1 - 13.18 below. The Laboratory shall designate and utilize qualified key personnel to perform these functions. A single individual may not

serve in more than two of the following supervisory positions, except for the Quality Assurance/Quality Control Officer position, which must be held by someone with no other responsibilities.

13.1 Laboratory Supervisor

13.2 Project Manager

13.3 Quality Assurance/Quality Control Officer

13.4 ICP Spectroscopist

13.5 ICP Operator

13.6 Flameless Atomic Absorption (AA) Spectroscopist

13.7 Flame and Cold Vapor Atomic Absorption Spectroscopist

13.8 Inorganic Sample Preparation Specialist

13.9 Classical Wet Chemical Techniques Analyst

13.10 Inorganic Chemist (Backup)

13.11 GC/MS Laboratory Supervisor

13.12 GC/MS/DS Operator

13.13 Systems Manager

13.14 Programmer Analyst

13.15 Mass spectral interpretation specialist

13.16 GC Laboratory Supervisor

13.17 Pesticide Residue Analysis Expert for organochlorine pesticides and PCBs

13.18 Purge and Trap Volatile Organics Analysis Expert

13.19 Sample Preparation Laboratory Supervisor

13.20 Sample Extraction/Concentration Specialist

13.21 Sample Custodian responsible for sample receipt, storage, and tracking, including chain-of-custody procedures.

13.22 Data Reporting and Delivery Officer

Additional Requirements

14.0 Information Requests

The Laboratory shall respond within seven days to written requests from data recipients for additional information or explanations that result from NYSDEC inspection activities unless otherwise specified in the contract or project work plan.

15.0 Unused Samples and Extracts

The Laboratory is required to retain unused sample volume and used sample containers for a period of 120 days after data submission. From time of receipt until disposal, the Laboratory shall maintain all samples and unused sample volumes stored at 4°C (±2°C), protected from light. Samples and unused sample volumes must be stored separately from sample extracts and standards.

The Laboratory shall preserve all sample extracts after analysis in bottles/vials with Teflon-lined septa and shall maintain stored extracts at 4°C (±2°C). The Laboratory is required to retain the sample extracts for 180 days after data submission. During that time, the Laboratory shall submit the extracts within 7 days after request, by the Project Officer or the Bureau of Watershed Assessment and Research as specified in Exhibit B.

16.0 Chain-of-Custody/Document Control Procedures

The Laboratory shall adhere to chain-of-custody and document control procedures described in Exhibit F. Documentation, as described therein, shall be required to show that all procedures are being strictly followed. This documentation shall be reported as the Complete SDG File Purge (see Exhibit B).

17.0 Sample Scheduling

Sample shipments to the Laboratory's facility will be scheduled by DEC Project Officers and coordinated by the Bureau of Watershed Assessment and Research (BWAR) acting on behalf of the Project Officer. The Laboratory shall communicate with BWAR personnel by telephone as necessary throughout the process of sample scheduling, shipment, analysis and data reporting, to ensure that samples are properly processed.

If there are problems with the samples (e.g., mixed media, containers broken or leaking) or sample documentation/paperwork (e.g., Contract Lab Sample Information Sheet not with shipment, sample bottle and Sample Information Sheet numbers do not correspond) the Laboratory shall immediately contact BWAR for resolution. The Laboratory shall immediately notify BWAR regarding any problems and laboratory conditions that affect the timeliness of analyses and data reporting. In particular, the Laboratory shall notify BWaR personnel, or the Project Officer in advance regarding sample data that will be delivered late and shall specify the estimated delivery date.

18.0 Sample Delivery Groups

Sample analyses will be scheduled by groups of samples, each defined as a Sample Delivery Group (SDG) and identified by a unique NYSDEC SDG number assigned by the Project Officer. An SDG signifies a group of samples collected at one site or geographical areas over a finite time period, and will include one or more field samples with associated blanks. Samples may be shipped to the Laboratory in a single shipment

or multiple shipments over a period of time, up to 7 days, depending on the size of the SDG.

A Sample Delivery Group (SDG) is defined by the following, whichever is most frequent, unless otherwise specified in a Project Workplan:

- all field samples received with the same SDG #, OR
- each 20 field samples within an SDG, OR
- each 7 day calendar period during which field samples in an SDG are received (said period beginning with the receipt of the first sample in the SDG).

All data (hardcopy and computer-readable format) for all samples in a Sample Delivery Group are due concurrently to all data recipients 30 days after receipt of the last sample received in the Sample Delivery Group. Data for all samples in a Sample Delivery Group must be submitted together (in one package) in the order specified in Exhibit B. The Sample Delivery Group number is identified on the Contract Lab Sample Information Sheet. The SDG number must be reported on all data reporting forms.

The SDG Receipt Date is the day the last sample in the SDG is received. Data for all samples in the SDG are due 30 days following this date.

The Laboratory is responsible for identifying each Sample Delivery Group as samples are received, through proper sample documentation (see Exhibit B) and communication with BWAR personnel.

19.0 Contract Lab Sample Information Sheets

Each sample received by the Laboratory will be labeled with a DEC sample number, and accompanied by a Contract Lab Sample Information Sheet form bearing the Case number, SDG number, sample number and descriptive information regarding the sample and a chain-of-custody sheet. The Laboratory shall complete and sign the chain-of-custody sheet, recording the date of sample receipt and sample condition on receipt for each sample container.

The Laboratory shall submit signed copies of Contract Lab Sample Information Sheets and the chain-of-custody forms for all samples in a Sample Delivery Group with the analytical report for that SDG. These sheets shall be submitted in Sample Delivery Group sets (i.e., all sheets for a Sample Delivery Group shall be clipped together) with an SDG Cover Sheet containing information regarding the Sample Delivery Group, as specified in Exhibit B.

20.0 Weekly Sample Submission Summary

The Laboratory shall submit, via e-mail, a Weekly Sample Submission Summary no later than the Wednesday following the week being reported. This information must be transmitted electronically as a Microsoft Excel compatible file. NYSDEC will provide the file structure.

21.0 Identifying Numbers

NYSDEC Case numbers, SDG numbers, and DEC sample numbers shall be used by the Laboratory in identifying samples received under this Protocol both verbally and in reports/correspondence.

22.0 Sample Shipments

Samples will routinely be shipped to the Laboratory through an overnight delivery service. However, as necessary, the Laboratory shall be responsible for any handling or processing required for the receipt of sample shipments, including pick-up of samples at the nearest servicing airport, bus station or other carrier service within the Laboratory's geographical area. The Laboratory shall be available to receive sample shipments at any time the delivery service is operating, including Saturdays.

23.0 Acceptance of Samples

The Laboratory shall accept all samples scheduled by DEC, provided that the total value of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Laboratory elect to accept additional samples, the Laboratory shall remain bound by all contract requirements for analysis of those samples accepted.

Section III - Detailed Technical And Management Requirements

As cited in Section II, the Laboratory shall have the following technical and management capabilities.

***NOTE**: For those technical functions which require a minimum educational degree and experience, an advanced degree in chemistry or any scientific/engineering discipline, (e.g., Master's or Doctorate) does not substitute for the minimum experience requirements.*

Any personnel changes affecting the key personnel as stated in Exhibit A, Section III, Items 1 and 2, the Laboratory shall notify in writing the Bureau of Watershed Assessment and Research (BWAR) within 14 days of the personnel change. The Laboratory shall provide a detailed resume to BWAR for the replacement personnel within 14 days of the Laboratory's assignment of the personnel. The resume shall include position description of titles, education (pertinent to this Protocol), number of years of experience (pertinent to this Protocol) month and year hired, previous experience and publications.

1.0 Technical Functions

1.1 Quality Assurance Officer

1.1.1 Responsible for overseeing the quality assurance aspects of the data and reporting directly to upper management to meet all terms and conditions of this Protocol.

1.1.2 Qualifications:

1.1.2.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.1.2.2 Experience:

Minimum of five years of environmental laboratory experience, including at least one year of applied experience with QA principles and practices in an analytical laboratory.

1.2 GC/MS Laboratory Supervisor

1.2.1 Responsible for all technical efforts of the GC/MS laboratory to meet all terms and conditions of this Protocol.

1.2.2 Qualifications:

1.2.2.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.2.2.2 Experience:

Minimum of three years of laboratory experience in operating a GC/MS, including at least one year of supervisory experience.

1.3 GC/MS Operator Qualifications

1.3.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.3.2 Experience:

One year of experience in operating and maintaining GC/MS/DS in conjunction with the educational requirement; or, in lieu of the educational requirement, three additional years of experience in operating and maintaining GC/MS/DS and interpreting GC/MS data.

1.4 Mass Spectral Interpretation Specialist Qualifications

1.4.1 Education:

1.4.1.1 Minimum of Bachelor's degree in chemistry or any physical science.

1.4.1.2 Training course(s) in mass spectral interpretation.

1.4.2 Experience:

Minimum of two years of experience in mass spectral interpretation.

1.5 GC Laboratory Supervisor

1.5.1 Responsible for all technical efforts of the GC Laboratory to meet all terms and conditions of this Protocol.

1.5.2 Qualifications:

1.5.2.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.5.2.2 Experience:

Minimum of three years of laboratory experience in operating a GC/EC, including at least one year of supervisory experience.

1.6 GC Operator

1.6.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.6.2 Experience:

One year of experience in operating and maintaining GC/EC in conjunction with the educational requirement; or, in lieu of the educational requirement, three additional years of experience in operating and maintaining GC/EC and interpreting GC/EC data.

1.7 Pesticide Residue Analysis Expert Qualifications

1.7.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.7.2 Experience:

Minimum of two years in operating and maintaining GC and interpreting GC chromatograms.

1.8 Organic Sample Preparation Laboratory Supervisor

1.8.1 Responsible for all technical efforts of sample preparation for organic analysis to meet all terms and conditions of the Protocol.

1.8.2 Qualifications:

1.8.2.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.8.2.2 Experience:

Minimum of three years of laboratory experience in organic sample preparation, including at least one year of supervisory experience.

1.9 Organic Extraction/Concentration Expert Qualifications

1.9.1 Education:

Minimum of high school diploma and a college level course in general chemistry or equivalent.

1.9.2 Experience:

Minimum of one year experience in extraction/concentration.

1.10 Organic Analysis Technical Staff Redundancy

The Laboratory shall have a minimum of one (1) chemist available at any one time as a back-up technical person with the following qualifications, to ensure continuous operations to accomplish the required work as specified by this Protocol.

1.10.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.10.2 Experience:

Minimum of one year experience in each of the following areas:

1.10.2.1 GC/MS operation and maintenance for volatiles and semivolatiles analyses.

1.10.2.2 Mass spectral interpretation.

1.10.2.3 Extraction

1.10.2.4 Pesticide/Aroclor analysis.

1.11 Inorganics Laboratory Supervisor

1.11.1 Responsible for all technical efforts of the Inorganics Laboratory to meet all terms and conditions of this Protocol.

1.11.2 Qualifications:

1.11.2.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.11.2.2 Experience:

Minimum of three years of laboratory experience, including at least one year in a supervisory position.

1.12 ICP Spectroscopist Qualifications

1.12.1 Education:

1.12.1.1 Minimum of Bachelor's degree in chemistry or any physical science.

1.12.1.2 Specialized training in ICP Spectroscopy.

1.12.2 Experience:

Minimum of two years of applied experience with ICP analysis of environmental samples.

1.13 ICP Operator Qualifications

1.13.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.13.2 Experience:

Minimum of one year of experience in operating and maintaining ICP instrumentation, in conjunction with the educational requirement; or, in lieu of the educational requirement, three additional years of experience in operating and maintaining ICP instrumentation.

1.14 Atomic Absorption (AA) Operator Qualifications

1.14.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.14.2 Experience:

Minimum of one year of experience in operating and maintaining AA instrumentation for each of the following AA techniques: (a) flame (if flame will be used), (b) graphite furnace, and (c) cold vapor, in conjunction with the educational requirement; or, in lieu of the educational requirement, three additional years of experience in operating and maintaining AA instrumentation, including flame, graphite furnace, and cold vapor techniques.

1.15 Metals/Wet-Chemistry Sample Preparation Laboratory Supervisor

1.15.1 Responsible for all technical efforts of metals and wet-chemical sample preparations to meet all terms and conditions of this Protocol.

1.15.2 Qualifications:

1.15.2.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.15.2.2 Experience:

Minimum of three years of laboratory experience, including at least one year of supervisory experience.

1.16 Inorganic Sample Preparation Specialist Qualifications

1.16.1 Education:

Minimum of high school diploma and a college level course in general chemistry or equivalent.

1.16.2 Experience:

Minimum of six months of experience in an analytical laboratory.

1.17 Classical Techniques (Wet-Chemical) Analyst Qualifications

1.17.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.17.2 Experience:

Minimum of six months of experience with classical chemistry laboratory procedures, in conjunction with the educational requirements; or, in lieu of the educational requirement, two years of additional equivalent experience.

1.18 System Manager

1.18.1 Responsible for the management and quality control of all computing systems (hardware, software, documentation and procedures), generating, updating, and quality controlling automated deliverables to meet all terms and conditions of this Protocol.

1.18.2 Qualifications:

1.18.2.1 Education:

Minimum of Bachelor's degree with four or more intermediate courses in programming, information management, database management systems, or systems requirements analysis.

1.18.2.2 Experience:

Minimum of three years experience in data or systems management or programming including one year of experience with the software being utilized for data management and generation of laboratory reports.

1.19 Programmer Analyst

1.19.1 Responsible for the installation, operation and maintenance of software and programs generating, updating, and quality controlling analytical databases and automated deliverables to meet all terms and conditions of this Protocol.

1.19.2 Qualifications:

1.19.2.1 Education:

Minimum of Bachelor's degree with four or more intermediate courses in programming, information management, database management systems, or systems requirements analysis.

1.19.2.2 Experience:

Minimum of three years experience in systems or applications programming including one year of experience with the software being utilized for data management and generation of laboratory reports.

1.20 Inorganic Technical Staff Redundancy

In order to ensure continuous operations to accomplish the required work as specified under this Protocol, the Laboratory shall have a minimum of one (1) chemist available at all times as a back-up technical person with the following qualifications:

1.20.1 Education:

Minimum of Bachelor's degree in chemistry or any physical science.

1.20.2 Experience:

Minimum of one year of experience in each of the following areas:

1.20.2.1 ICP operation and maintenance.

1.20.2.2 AA operation and maintenance.

1.20.2.3 Classical chemistry analytical procedures.

1.20.2.4 Sample preparation for metals/wet-chemical analysis.

1.21 Sample Custodian

1.21.1 Education:

Minimum of high school diploma or equivalency diploma.

1.21.2 Experience:

One year of general laboratory experience.

2.0 Facilities

The adequacy of the facilities and equipment is of equal importance as the technical staff to accomplish the required work as specified by this Protocol.

2.1 Sample Receipt Area

Adequate, contamination-free, well-ventilated work space provided with chemical resistant bench top and fume hood for receipt and safe handling of NYSDEC samples.

2.2 Secure Storage Area

Sufficient locked refrigerator space to maintain unused NYSDEC sample volume for 90 days after data submission and sample extracts for 90 days after data submission. Samples must be stored in an atmosphere demonstrated to be free from all potential contaminants. **NOTE**: Volatile samples must be stored in a refrigerator used only for storage of volatile samples submitted under this Protocol. Samples, sample extracts, and standards must be stored separately to prevent cross contamination. Semivolatile and pesticide/Aroclor standards and extracts must be stored separately from volatile standards and extracts. Inorganic samples and digestates must be stored securely and separately from organic samples. Area access must be restricted to sample custodians.

2.3 Sample Preparation Area

The sample preparation area shall be separate and isolated from the volatile analysis area. It shall have adequate, contamination-free, well-ventilated work space provided with:

2.3.1 Benches with chemical resistant tops and exhaust hoods. **NOTE**: Standards must be prepared in a glove box or isolated area.

2.3.2 Source of distilled or demineralized organic-free water.

2.3.3 Analytical balance(s) located away from draft and rapid change in temperature.

3.0 Instrumentation

At a minimum, the Laboratory shall have the instruments listed in Table 1.1 operative at the time of the on-site laboratory audit and committed for the full duration of any project to be performed under this Protocol.

4.0 Data Management and Handling

4.1 Hardware - Laboratory shall have an IBM or IBM-compatible mini-computer or PC capable of recording required sample data on 3.5 inch double-sided, double-density 1.44 M-byte diskettes in ASCII text file format and in accordance with the file, record and field specifications listed in Protocol, Exhibit H.

Other minimum requirements include:

- Hard disk of at least 20 M-bytes.
- Asynchronous, Hayes-compatible modem capable of at least 2,400 baud transmission speed. In addition, MNP level 5 compatibility is recommended.
- Modem capable of at least 2,400 baud transmission speed which is compatible with the EPA Telecommunications Network.

Table 1.1

Fraction	No. of Instruments	Type of Instrument
Volatiles	2	GC/MS/DS with purge and trap device
Low Concentration Volatiles	1	Dedicated GC/MS/DS with purge and trap device
Volatiles	2	GC/HECD/PID with dual column
Semivolatiles (BNA)	2	GC/MS/DS
Pesticides/Aroclors	2	GC/EC with dual column
ICP Metals	2	EITHER ICP Emission Spectrophotometer AND/OR Flame Atomic Absorption Spectrophotometer
Graphite Furnace AA Metals	2	Atomic Absorption Spectrophotometer with Graphite Furnace Atomizer or Axial ICP or ICP-MS or any redundant combination
Mercury	2	Mercury Cold Vapor AA Analyzer or AA Instrument modified for Cold Vapor Analysis

4.2 Software - Software, utilized in generating, updating and quality controlling analytical databases and automated deliverables shall have the following additional capabilities:

- Editing and updating databases.

- QC of automated deliverables.

- Controlled access using user ID and file password protection.

4.3 The Laboratory shall also be able to submit reports and data packages as specified in Exhibit B of this Protocol. To complete this task, the Laboratory shall be required to provide space, tables and adequate copy machines to meet the Protocol requirements.

5.0 Laboratory Management Capability

The Laboratory must have an organization with well-defined responsibilities for each individual in the management system to ensure sufficient resources for the NYSDEC contract or project(s) and to maintain a successful operation. To establish this capability, the Laboratory shall designate personnel to carry out the following responsibilities for the NYSDEC contract or project(s). Functions include, but are not limited to, the following:

5.1 Technical Staff

Responsible for all technical efforts for the NYSDEC contract or project(s). The Laboratory shall have adequate number of technical personnel to meet the requirements of this Protocol.

5.2 Project Manager

Responsible for overall aspects of NYSDEC contract or project(s) (from sample receipt through data delivery) and shall be the primary contact for the Bureau of Watershed Assessment and Research or Project Officers.

5.3 Sample Custodian

Responsible for receiving the NYSDEC samples (logging, handling and storage).

5.4 Quality Assurance Officer

Responsible for overseeing the quality assurance aspects of the data and reporting directly to upper management.

5.5 Document Control Officer

Responsible for all aspects of data deliverables: organization, packaging, copying, and delivery. Responsible for ensuring that all documents generated are placed in the Complete SDG File for inventory and are delivered to the appropriate NYSDEC Regional personnel or other receiver.

EXHIBIT B

Reporting and Deliverables Requirements

Exhibit B

Table of Contents

Section I -- Contract Reports/Deliverables Distribution

The following table details the Protocol reporting deliverables requirements and specifies the distribution that is required for each deliverable.

***NOTE**: Specific recipient names and addresses are subject to change during the term of the contract. The Bureau of Watershed Assessment and Research (BWAR) will notify the Laboratory in writing of such changes when they occur.*

Item		No. of Copies	Delivery Schedule	Distribution (1)	(2)	(3)
A.	Standard Operating Procedures	1	60 days after notification of contract award, and as required in Exhibit E.	X		
B.	Quality Assurance Plan	1	60 days after notification of contract award, and as required in Exhibit E.	X		
C.	Weekly Sample Receipt Summary	1	Wednesday following the week covered by the report	X		
*D.	Sample Data Summary Package	2	30 days after receipt of last sample in Sample Delivery Group (SDG)**		X	X
*E.	Sample Data Package	2	30 days after receipt of last sample in SDG		X	X
*F.	Data in Computer-Readable Form	1	30 days after receipt of last sample in SDG	X		
G.	GC/MS Tapes	Lot	Retain for 365 days after data submission, or submit within 7 days after receipt of written request by BWAR	As Directed		

Item		No. of Copies	Delivery Schedule	Distribution (1) (2) (3)
H.	Extracts	Lot	Retain for 90 days after data submission or submit within 7 days after receipt of written request by BWAR	As Directed
*I.	Complete SDG File Purge	1 Pkg	30 days after receipt of last sample in Sample Delivery Group	X
J.	Semiannual Verification of Instrument Parameters	1	Semiannually: 15th day of January, July	X

* Concurrent delivery required. Delivery shall be made such that all designated recipients receive the item on the same calendar day.

** Sample Delivery Group (SDG) is a group of samples within a Case, received over a period of 7 days or less and not exceeding 20 samples. Data for all samples in the SDG are due concurrently, unless specified otherwise in a project workplan. (See Exhibit A, for further description).

***NOTE**: As specified in the Protocol unless otherwise instructed by the BWAR the Laboratory shall dispose of unused sample volume and used sample bottles/containers no earlier than ninety (90) days following submission of analytical data.*

Distribution Addresses:

(1) Analytical Services Section
Bureau of Program Services and Research
NYS Department of Environmental Conservation
50 Wolf Road, Room 392
Albany, New York 12233-3502

(2) NYSDEC Sample Submitters

(3) NYSDEC Project Officers

The BWAR acting on behalf of the Project Officer, will provide the Laboratory with the list of addressees for the nine NYSDEC Regions. BWAR will provide the Laboratory with updated Regional address/name lists as necessary throughout the period of the contract and identify other client recipients on a case-by-case basis.

Section II -- Report Descriptions and Order of Data Deliverables

The Laboratory shall provide reports and other deliverables as specified in Section I. The required content and form of each deliverable is described in this Exhibit.

All reports and documentation MUST BE as follows:

- Legible,
- Clearly labeled and completed in accordance with instructions in this Exhibit,
- Arranged in the order specified in this Section, and
- Paginated consecutively in ascending order starting from the SDG Narrative.

If submitted documentation does not conform to the above criteria, the Laboratory will be required to resubmit such documentation with deficiency(ies) corrected, at no cost to NYSDEC.

Whenever the Laboratory is required to submit or resubmit data as a result of an on-site laboratory evaluation or through a Bureau of Watershed Assessment and Research (BWAR) action, or through a Project Directors request, the data must be clearly marked as ADDITIONAL DATA and sent to all Protocol specified data recipients. A cover letter shall be included which describes what data is being delivered, to which NYSDEC sample(s) it pertains, and who requested the data.

Sections IV and VI of this Exhibit contain copies of the required data reporting forms in Agency-specified formats, along with instructions to assist the Laboratory in accurately providing NYSDEC all required data. Data elements with field parameters for reporting data in computer readable form are contained in Exhibit H.

Descriptions of the requirements for each deliverable item cited in Section I, Contract Reports/Deliverables Distribution Schedule are specified in parts A-G of this Section. Items submitted concurrently MUST BE arranged in the order listed. Additionally, the components of each item MUST BE arranged in the order presented in this Section when the item is submitted.

Examples of specific data deliverables not included herein may be obtained by submitting a written request to the Bureau of Watershed Assessment and Research, stating the information requested, and signed by the Laboratory Manager.

A. - Standard Operating Procedures

See Exhibits E and F for requirements

B. - Quality Assurance Plan

See Exhibits E and F for requirements

C. - Weekly Sample Receipt Summary

Weekly Sample Receipt Summaries shall be submitted by the Wednesday following the week for which they are submitted. This information must be transmitted electronically as a Microsoft Excel compatible file. NYSDEC will provide the file structure.

The Weekly Sample Receipt Summary shall contain the following items:

- Lab name
- Contract number
- NYSDEC Case #
- NYSDEC SDG #
- NYSDEC Sample ID #
- Lab ID #
- Name of NYSDEC Sample Submitter
- Code numbers for requested analyses from Contract Laboratory Sample Information Sheet
- Sample Analysis Price - full sample price from contract for each sample # reported.
- List of NYSDEC sample numbers of all samples in the SDG, identifying the first and last samples received, and their dates of receipt.

***NOTE**: When more than one sample is received in the first or last SDG shipment, the "first" sample received would be the lowest sample number (considering both alpha and numeric designations); the "last" sample received would be the highest sample number (considering both alpha and numeric designations).*

The NYSDEC SDG# is found on the Contract Laboratory Sample Information Sheet. (The SDG number is also reported on all data reporting forms. See Section III, Forms Instruction Guide.)

D. - Sample Data Summary Package

As specified in the Delivery Schedule, one Sample Data Summary Package each shall be delivered to BWAR and the sample collector concurrently with delivery of other required sample data. The Sample Data Summary Package consists of copies of specified items from the Sample Data Package. These items are listed below and described under part C, Sample Data Package.

The Sample Data Summary Package shall be ordered as follows and shall be submitted separately (i.e., separated by rubber bands, clips or other means) directly preceding the Sample Data Package. Sample data forms shall be arranged in increasing NYSDEC sample number order, considering both letters and numbers. E400 is a lower sample number than RH100, as E precedes R in the alphabet.

The Sample Data Summary Package shall contain all data for all samples within one Sample Delivery Group of the Case as follows:

1. NYSDEC Data Package Summary Forms
2. SDG Narrative

3. By fraction (VOA, SV, PEST, INORG, CONV) and by sample within each fraction - tabulated target compound results (Form I-ORG or Form I-IN) and tentatively identified compounds (Form I-ORG, TIC) (VOA and BNA only)

4. By fraction (VOA, SV, and PEST) - surrogate spike analysis results (Form II-ORG) by matrix (water and/or soil) and for soil, by concentration (low or medium)

5. By fraction (VOA, SV, and PEST) - matrix spike/matrix spike duplicate/matrix spike blank results (Form III-ORG) - as required by method.

6. By fraction (VOA, SV, and PEST) - QC Check Sample/Standard Recovery Summary - If required by method.

7. By fraction (INORG and CONV only) - duplicate sample results (Form VI-IN)

8. By fraction (INORG and CONV only) - spike sample results (Form V-IN)

9. By fraction (VOA, SV, PEST, INORG, CONV) - blank data (Form IV-ORG and Form III-IN) and tabulated results (Form I-ORG and Form I-IN) including tentatively identified compounds (Form I-ORG, TIC)(VOA and BNA only).

10. By fraction (VOA and SV only) - internal standard area data (Form VIII-ORG).

E. - Sample Data Package

The Sample Data Package is divided into the eight major units described below. The last six units are each specific to an analytical fraction (volatiles, semivolatiles, pesticides/Aroclors, GC organics, inorganics, and conventional wet-chemistry). If the analysis of a fraction is not required, then that fraction-specific unit is not required as a deliverable.

The Sample Data Package shall include data for analyses of all samples in one Sample Delivery Group, including field samples, reanalyses, blanks, duplicates, spikes, matrix spikes, matrix spike duplicates, and matrix spike blanks.

All data produced in support of Superfund investigations/remediations as identified by checked boxes under the Contract Laboratory Section of the Contract Laboratory Sample Information Sheet (See Exhibit A)shall be reported as specified for the Superfund Category (paragraph 1.). All data generated in support of the SPDES program as identified by a CASE # beginning with the letter "E" shall be reported using ASP Category-B (paragraph 3.). All other samples shall be reported using either ASP Category A or ASP Category B described in paragraphs 2. and 3. The specific reporting level to be used shall be specified by the Contract Laboratory Sample Information Sheet, unless otherwise specified in a project workplan.

The Laboratory shall retain a copy of the Sample Data Package for 365 days after final acceptance of data. After this time, the Laboratory may dispose of the package.

1.0 Superfund Category

1.1 SDG Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: Laboratory name; Case number; Sample Delivery Group number (SDG); sample numbers in the SDG, differentiating between initial analyses and re-analyses; Contract number; and detailed documentation of any quality control, sample, shipment and/or analytical problems encountered in processing the samples reported in the data package.

Whenever data from sample re-analysis are submitted, the Laboratory shall state in the SDG Narrative for each re-analysis, whether it considers the re-analysis to be billable, and if so, why.

The Laboratory must also include any problems encountered: both technical and administrative, corrective actions taken, and resolution and an explanation for all flagged edits (i.e., manual edits) on quantitation lists.

The SDG Narrative shall contain the following statement, verbatim: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on floppy diskette has been authorized by the Laboratory Manager or his designee, as verified by the following signature." This statement shall be directly followed by signature of the Laboratory Manager or his designee with a typed line below it containing the signer's name and title, and the date of signature.

Additionally, the SDG Narrative itself must be signed in original signature by the Laboratory Manager or his designee and dated.

1.2 Contract Lab Sample Information Sheets

A copy of the Contract Lab Sample Information Sheets (CLSIS) for all of the samples in the SDG. The CLSIS shall be arranged in increasing NYSDEC sample number order, considering both letters and numbering in ordering samples.

1.3 Chain-of-Custody Forms

Copies of both the external and internal chain-of-custody sheets for all samples within the SDG.

1.4 Superfund-CLP Volatiles Data

1.4.1 QC Summary

1.4.1.1 System Monitoring Compound Summary (Form II-CLP-VOA)

1.4.1.2 Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Summary (Form III-CLP-VOA)

1.4.1.3 Method Blank Summary (Form IV-CLP-VOA)

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank, by instrument.)

1.4.1.4 GC/MS Instrument Performance Check (Form V-CLP-VOA).

BFB in chronological order; by instrument.

1.4.1.5 Internal Standard Area and RT Summary (Form VIII-CLP-VOA)

In chronological order; by instrument.

1.4.1.6 Instrument Detection Limits

1.4.2 Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I-CLP-VOA, including Form I-CLP-VOA-TIC), followed by the raw data for volatile samples. These sample packets should then be placed in increasing NYSDEC sample number order, considering both letters and numbers in ordering samples.

1.4.2.1 Target Compound Results - Organic Analysis Data Sheet (Form I-CLP-VOA).

Tabulated results (identification and quantitation) of the specified Superfund-CLP target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the SDG Narrative (reference C.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

On Form I-CLP-VOA, the appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable.

***NOTE**: Report analytical results to one significant figure if the value is less than 10; to two significant figures above 10.*

1.4.2.2 Tentatively Identified Compounds (Form I-CLP-VOA-TIC).

This form must be included even if no compounds are found. If so, indicate this on the form by entering "0" in the field for "Number found".

Form I-CLP-VOA-TIC is the tabulated list of the highest probable match for up to 10 organic compounds not system monitoring compounds and are not listed in Exhibit C (Superfund-TCL) for the appropriate program under which the samples were submitted, including the CAS (Chemical Abstracts Registry) number, tentative identification and estimated concentrations. For estimating concentration, assume a response factor of 1, and estimate

the concentration by comparison of the compound peak height or total area count to the peak height or total area count of the nearest internal standard free of interferences on the reconstructed ion chromatogram.

***NOTE**: The Laboratory must be consistent, i.e., use peak height for all comparisons or use total area count for all comparisons.*

1.4.2.3 Reconstructed Total Ion Chromatograms (RIC) for each sample or sample extract.

RICs must be normalized to the largest non-solvent component and contain the following header information:

- NYSDEC sample number
- Date and time of analysis
- GC/MS instrument ID
- Lab file ID

Internal standard and system monitoring compounds are to be labeled with the names of compounds, either directly out from the peak, or on a print-out of retention times if retention times are printed over the peak.

If automated system procedures are used for preliminary identification and/or quantification of the Superfund Target Compound List (Superfund-TCL) compounds, the complete data system report must be included in all sample data packages in addition to the reconstructed ion chromatogram. The complete data system report shall include all of the information listed below. For laboratories which do not use the automated data system procedures, a laboratory "raw data sheet", which contains the following information, must be included in the sample data package in addition to the chromatogram.

- NYSDEC sample number
- Date and time of analysis
- RT or scan number of identified Superfund-TCL compounds
- Ion used for quantitation with measured area
- Copy of area table from data system
- GC/MS instrument ID
- Lab file ID

In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report.

1.4.2.4 For each sample, by each compound identified, the following shall be included in the data package:

1.4.2.4.1 Copies of raw spectra and copies of background-subtracted mass spectra of target compounds listed in Exhibit C (Superfund-TCL) that are identified in the sample and corresponding background-subtracted TCL standard mass spectra. Spectra must be labeled with NYSDEC sample number, lab file ID, date and time of analysis, and GC/MS instrument ID; compound names must be clearly marked on all spectra.

1.4.2.4.2 Copies of mass spectra of organic compounds not listed in Exhibit C (Superfund-TCL) (Tentatively Identified Compounds), with associated best-match spectra (three best matches), labeled as in 1.4.2.4.1 above.

1.4.3 Standards Data

1.4.3.1 Initial Calibration Data (Form IV-CLP-VOA) - in order by instrument if more than one instrument used.

1.4.3.1.1 VOA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for the initial (five point) calibration, labeled as in 1.4.2.3 above. Spectra are not required.

1.4.3.1.2 All initial calibration data that pertain to samples in the data package must be included, regardless of when it was performed and for which case. When more than one initial calibration is performed, the data must be put in chronological order, by instrument.

1.4.3.2 Continuing Calibration (Form VII-CLP-VOA) - in order by instrument, if more than one instrument used.

1.4.3.2.1 VOA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for all continuing (12 hour) calibrations, labeled as in 1.4.2.3. Spectra are not required.

1.4.3.2.2 When more than one continuing calibration is performed, forms must be in chronological order, within fraction and instrument.

1.4.4 Raw QC Data

1.4.4.1 BFB (for each 12-hour period, for each GC/MS system utilized)

1.4.4.1.1 Bar graph spectrum, labeled as in 1.4.2.3.

1.4.4.1.2 Mass listing, labeled as in 1.4.2.3.

1.4.4.1.3 Reconstructed total ion chromatogram (RIC), labeled as in 1.4.2.3.

1.4.4.2 Blank Data - in chronological order.

***NOTE**: This order is different from that used for samples.*

1.4.4.2.1 Tabulated results (Form I-CLP-VOA)

1.4.4.2.2 Tentatively Identified Compounds (Form I-CLP-VOA-TIC) - even if none found.

1.4.4.2.3 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 1.4.2.3.

1.4.4.2.4 Superfund-TCL spectra with lab generated standard, labeled as in 1.4.2.4. Data systems which are incapable of dual display shall provide spectra in the following order:

- Raw Superfund-TCL compound spectra
- Enhanced or background subtracted spectra
- Laboratory generated Superfund-TCL standard spectra

1.4.4.2.5 GC/MS library search spectra for Tentatively Identified Compounds (TIC), labeled as in 1.4.2.4.

1.4.4.2.6 Quantitation/Calculation of Tentatively Identified Compound(s) (TIC) concentrations

1.4.4.3 Matrix Spike Blank Data

1.4.4.3.1 Tabulated results (Form I-CLP-VOA) of all Superfund-TCL compounds. Form I-CLP-VOA-TIC is required.

1.4.4.3.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 1.4.2.4. Spectra are required.

1.4.4.4 Matrix Spike Data

1.4.4.4.1 Tabulated results (Form I-CLP-VOA) of all Superfund-TCL compounds. Form I-CLP-VOA-TIC is <u>not</u> required.

1.4.4.4.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 1.4.2.4. Spectra are <u>not</u> required.

1.4.4.5. Matrix Spike Duplicate Data

1.4.4.5.1 Tabulated results (Form I-CLP-VOA) of all Superfund-TCL Compounds. Form I-CLP-VOA-TIC is <u>not</u> required.

1.4.4.5.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.3.2.4. Spectra are not required.

1.4.5 Copy of Calculations

The Laboratory must provide a copy of the calculations work sheet showing how final results are obtained from values printed on the quantitation report. If manipulations are performed by a software package, a copy of the formula used must be supplied as well as values for all terms in the formula.

1.4.6 Copy of Extraction Logs

These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. matrix spike, matrix spike duplicate, matrix spike blank) correspond to each batch extracted, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) final volumes and vial identification numbers.

1.5 Superfund-CLP Semivolatiles Data

1.5.1 QC summary

1.5.1.1 Surrogate Percent Recovery Summary (Form II-CLP-SV)

1.5.1.2 Matrix Spike/Matrix Spike Duplicate Summary (Form III-CLP-SV)

1.5.1.3 Method Blank Summary (Form IV-CLP-SV)

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank.)

1.5.1.4 GC/MS Instrument Performance Check (Form V-CLP-SV).

DFTPP in chronological order; by instrument.

1.5.1.5 Internal Standard Area and RT Summary (Form VIII-CLP-SV).

1.5.1.6 Instrument Detection Limits.

1.5.2 Sample Data.

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I-CLP-SV, including Form I SV-TIC), followed by the raw data for semivolatile samples. These sample packets should then be placed in increasing DEC sample number order, considering both letters and numbers in ordering samples.

1.5.2.1 TCL Results - Organic Analysis Data Sheet (Form I-CLP-SV-1, SV-2).

Tabulated results (identification and quantitation) of the specified Superfund-CLP target compounds (Exhibit C). The validation and release

of these results is authorized by a specific, signed statement in the SDG Narrative (reference C.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

On Form I-CLP-SV-1,-SV-2, the appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable.

***NOTE**: Report analytical results to one significant figure if the value is less than 10; to two significant figures above 10.*

1.5.2.2 Tentatively Identified Compounds (Form I-CLP-SV-TIC)

This form must be included even if no compounds are found. If so, indicate this on the form by entering "0" in the field for "Number found".

Form I-CLP-SV-TIC is the tabulated list of the highest probable match for up to 20 of the nonsurrogate organic compounds not listed in Exhibit C (Superfund-TCL). It includes the CAS (Chemical Abstracts Registry) number, tentative identification and estimated concentration. For estimating concentration, assume a response factor of 1, and estimate the concentration by comparison of the compound peak height or total area count to the peak height or total area count of the nearest internal standard free of interferences on the reconstructed ion chromatogram.

***NOTE**: The Laboratory must be consistent, i.e., use peak height for all comparisons <u>or</u> use total area count for all comparisons.*

1.5.2.3 Reconstructed total ion chromatograms (RIC) for each sample, sample extract, standard, blank, and spiked sample.

RICs must be normalized to the largest nonsolvent component, and must contain the following header information:

- NYSDEC sample number
- Date and time of analysis
- GC/MS instrument ID
- Lab file ID

Internal standard and surrogate spiking compounds are to be labeled with the names of compounds, either directly out from the peak, or on a print-out of retention times if retention times are printed over the peak.

If automated data system procedures are used for preliminary identification and/or quantification of the Superfund Target Compound List (Superfund-TCL) compounds, the complete data system report must be included in all sample data packages, in addition to the reconstructed ion chromatogram. The complete data system report shall include all of the information listed below. For laboratories which do not use the automated data system procedures, a laboratory "raw data sheet," containing the following

information, must be included in the sample data package in addition to the chromatogram.

- NYSDEC sample number
- Date and time of analysis
- RT or scan number of identified Superfund-TCL compounds
- Ion used for quantitation with measured area
- Copy of area table from data system
- GC/MS instrument ID
- Lab file ID

In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report.

1.5.2.4 For each sample, by each compound identified, the following shall be included in the data package:

1.5.2.4.1 Copies of raw spectra and copies of background-subtracted mass spectra of target compounds listed in Exhibit C (Superfund-TCL) that are identified in the sample and corresponding background-subtracted Superfund-TCL standard mass spectra. Spectra must be labeled with NYSDEC sample number, lab file ID, date and time of analysis, and GC/MS instrument ID; compound names must be clearly marked on all spectra.

1.5.2.4.2 Copies of mass spectra of nonsurrogate organic compounds not listed in Exhibit C (Superfund-TCL) (Tentatively Identified Compounds) with associated best-match spectra (three best matches), labeled as in 1.5.2.4.1.

1.5.2.4.3 GPC chromatograms (if GPC performed).

1.5.3 Standards Data

1.5.3.1 Initial Calibration Data (Form VI-CLP-SV-1, SV-2) - in order by instrument, if more than one instrument used.

1.5.3.1.1 Semivolatile standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for the initial (five point) calibration, labeled in 1.5.2.3. Spectra are not required.

1.5.3.1.2 All initial calibration data that pertain to samples in the data package must be included, regardless of when it was performed and for which SDG. When more than one initial

calibration is performed, the data must be put in chronological order, by instrument.

1.5.3.2 Continuing calibration (Form VII-CLP-SV-1, SV-2) - in order by instrument, if more than one instrument used.

1.5.3.2.1 Semivolatile standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for all continuing (12 hour) calibrations, labeled as in 1.5.2.3. Spectra are not required.

1.5.3.2.2 When more than one continuing calibration is performed, forms must be in chronological order, by instrument.

1.5.3.3 Semivolatile GPC Calibration Data - UV detector traces showing peaks that correspond to the compounds in the semivolatile GPC calibration mixture. Traces must be labeled with GPC column identifier, date of calibration, and with compound names labeled either directly out from the peak, or on a printout of retention times, if retention times are printed over the peak. Do not include Form IX Pest-2, as the compounds used on that form are not appropriate for semivolatile sample extracts.

1.5.4 Raw QC Data

1.5.4.1 DFTPP (for each 12-hour period, for each GC/MS system utilized)

1.5.4.1.1 Bar graph spectrum, labeled as in 1.5.2.3.

1.5.4.1.2 Mass listing, labeled as in 1.5.2.3.

1.5.4.1.3 Reconstructed total ion chromatogram (RIC), labeled as in 1.5.2.3.

1.5.4.2 Blank Data - in chronological order by extraction date.

NOTE: *This order is different from that used for samples.*

1.5.4.2.1 Tabulated results (Form I-CLP-SV-1, SV-2)

1.5.4.2.2 Tentatively Identified Compounds (Form I-CLP-SV-TIC) - even if none found.

1.5.4.2.3 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 1.5.2.3.

1.5.4.2.4 Superfund-TCL spectra with lab generated standard, labeled as in 1.4.2.4. Data systems which are incapable of dual display shall provide spectra in order:

- Raw Superfund-TCL compound spectra
- Enhanced or background subtracted spectra

- Laboratory generated Superfund-TCL standard spectra

1.5.4.2.5 GC/MS library search spectra for Tentatively Identified Compounds (TIC), labeled as in 1.5.2.4.

1.5.4.2.6 Quantitation/Calculation of Tentatively Identified Compound(s) (TIC) concentrations

1.5.4.3 Matrix Spike Blank Data

1.5.4.3.1 Tabulated results (Form I-CLP-SV-1, SV-2) of all Superfund-TCL compounds. Form I-CLP-SV-TIC not required.

1.5.4.3.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 1.5.2.3. Spectra are required.

1.5.4.4 Matrix Spike Data

1.5.4.4.1 Tabulated results (Form I-CLP-SV-1, SV-2) of all Superfund-TCL compounds. Form I-CLP-SV-TIC not required.

1.5.4.4.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 1.5.2.3. Spectra are not required.

1.5.4.5 Matrix Spike Duplicate Data

1.5.4.5.1 Tabulated results (Form I-CLP-SV-1, SV-2) of all Superfund-TCL compounds. Form I-CLP-SV-TIC not required.

1.5.4.5.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 1.5.2.3. Spectra are not required.

1.5.5 Copy of Calculations

The Laboratory must provide a copy of the calculations work sheet showing how final results are obtained from values printed on the quantitation report. If manipulations are performed by a software package, a copy of the formula used must be supplied as well as values for all terms in the formula.

1.5.6 Copy of Extraction Logs

These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. matrix spike, matrix spike duplicate, matrix spike blank) correspond to each batch extracted, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) final volumes and vial identification numbers.

1.6 Superfund-CLP Pesticide/Aroclor Data

1.6.1 QC Summary

1.6.1.1 Surrogate Percent Recovery Summary (Form II-CLP-PEST)

1.6.1.2 Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Summary (Form III-CLP-PEST)

1.6.1.3 Method Blank Summary (Form IV-CLP-PEST)

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank.)

1.6.1.4 Instrument Detection Limits

1.6.2 Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I-CLP-PEST), followed by the raw data for pesticide samples. These sample packets should then be placed in increasing NYSDEC sample number order, considering both letters and numbers in ordering samples.

1.6.2.1 Superfund-TCL Results - Organic Analysis Data Sheet (Form I-CLP-PEST).

Tabulated results (identification and quantitation) of the specified Superfund target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the SDG Narrative (reference E.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

On Form I-CLP-PEST, the appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable. **NOTE**: Report analytical results to two significant figures for all pesticide/Aroclor samples.

1.6.2.2 Copies of pesticide chromatograms.

All chromatograms must be labeled with the following information.

- NYSDEC sample number.
- Volume injected (µL).
- Date and time of injection.
- GC column identification (by stationary phase and internal diameter).
- GC instrument identification.

- Positively identified compounds must be labeled with the names of compounds, either directly out from the peak, or on a print-out of retention times if retention times are printed over the peak.

1.6.2.3 Copies of pesticide chromatograms from second GC column confirmation. Chromatograms to be labeled as in 1.6.2.2 above.

1.6.2.4 GC integration report or data system printout.

1.6.2.5 Manual work sheets.

1.6.2.6 If pesticide/Aroclors are confirmed by GC/MS, the Laboratory shall submit copies of reconstructed ion chromatograms, raw spectra and copies of background-subtracted mass spectra of Superfund target compounds listed in Exhibit C (Superfund-TCL) that are identified in the sample and corresponding background-subtracted Superfund-TCL standard mass spectra. Compound names must be clearly marked on all spectra. For multicomponent pesticides/Aroclors confirmed by GC/MS, the Laboratory shall submit mass spectra of 3 major peaks of multicomponent compounds from samples and standards.

1.6.3 Standards Data

1.6.3.1 Initial Calibration of Single Component Analytes (Form VI-CLP-PEST-1 and PEST-2) - all GC columns, all instruments, in chronological order by GC column and instrument.

1.6.3.2 Initial Calibration of Multicomponent Analytes (Form VI-CLP-PEST-3) - all GC columns, all instruments, in chronological order by GC column and instrument

1.6.3.3 Analyte Resolution Summary (Form VI CLP-PEST-4) - all GC columns and instruments, in chronological order by GC column and instrument.

1.6.3.4 Calibration Verification Summary (Form VII CLP-PEST-1) - for all Performance Evaluation Mixtures and Instrument blanks, on all GC columns and instruments, in chronological order by GC column and instrument.

1.6.3.5 Calibration Verification Summary (Form VII CLP-PEST-2) - for all mid point concentrations of Individual Standard Mixtures A and B and Instrument blanks used for calibration verification, on all GC columns and instruments, in chronological order by GC column and instrument.

1.6.3.6 Analytical Sequence (Form VIII CLP-PEST) - all GC columns and instruments, in chronological order by GC column and instrument.

1.6.3.7 Florisil Cartridge Check (Form IX CLP-PEST-1) - for all lots of cartridges used to process samples in the SDG.

1.6.3.8 Pesticide GPC Calibration (Form IX CLP-PEST-2) - all GPC columns, in chronological order by calibration date.

1.6.3.9 Pesticide Identification Summary for Single Component Analytes (Form X CLP-PEST-1) - for all samples with positively identified single component analytes, in order by increasing NYSDEC sample number.

1.6.3.10 Pesticide Identification Summary for Multicomponent Analytes (Form X CLP-PEST-2) - for all samples with positively identified multicomponent analytes, in order by increasing NYSDEC sample number.

1.6.3.11 Chromatograms and data system printouts are required for all standards including the following:

- Resolution Check Mixture.
- Performance Evaluation Mixtures, all.
- Individual Standard Mixture A, at three concentrations, each initial calibration.
- Individual Standard Mixture B, at three concentrations, each initial calibration.
- All multicomponent analytes (Toxaphene and Aroclors), each initial calibration.
- All mid point concentrations of Individual Standard Mixtures A and B used for calibration verification.
- Florisil cartridge check solution, all lots.
- Pesticide GPC Calibration Check Solution, all calibrations relating to samples in the SDG.
- All multicomponent analyte standards analyzed for confirmation.

1.6.3.12 A printout of retention times and corresponding peak areas or peak heights must accompany each chromatogram. In addition, all chromatograms are required to be labeled with the following:

- NYSDEC Sample Number for the standard, i.e., INDA1, INDA2, etc. (See Forms Instructions for details).
- Label all standard peaks for all individual compounds either directly out from the peak or on the printout of retention times if retention times are printed over the peak.
- Total nanograms injected for each standard.
- Date and time of injection.
- GC column identification (by stationary phase and internal diameter).
- GC instrument identification.

1.6.3.13 Pesticide GPC Calibration Data - UV detector traces showing peaks that correspond to the compounds in the pesticide GPC calibration mixture. Traces must be labeled with GPC column identifier, date of calibration, and with compound names labeled either directly out from the peak, or on a printout of retention times, if retention times are printed over the peak.

1.6.4 Raw QC Data

1.6.4.1 Blank Data - in chronological order, by type of blank (method, instrument, sulfur cleanup).

***NOTE**: This order is different from that used for samples.*

1.6.4.1.1 Tabulated results (Form I-CLP-PEST).

1.6.4.1.2 Chromatogram(s) and data system printout(s) (GC) for each GC column and instrument used for analysis, labeled as in 1.6.2.2 above.

1.6.4.2 Matrix Spike Data

1.6.4.2.1 Tabulated results (Form I-CLP-PEST) of all Superfund-TCL compounds.

1.6.4.2.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 1.6.2.2 above.

1.6.4.3 Matrix Spike Duplicate Data

1.6.4.3.1 Tabulated results (Form I-CLP-PEST) of all Superfund-TCL compounds.

1.6.4.3.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 1.6.2.2 above.

1.6.4.4 Matrix Spike Blank Data

1.6.4.4.1 Tabulated results (Form I-CLP-PEST) of all Superfund-TCL compounds.

1.6.4.4.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 1.6.2.2 above.

1.6.5 Copy of Calculations

The Laboratory must provide a copy of the calculations work sheet showing how final results are obtained from values printed on the quantitation report. If manipulations are performed by a software package, a copy of the formula used must be supplied as well as values for all terms in the formula.

1.6.6 Copy of Extraction Logs

These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. matrix spike, matrix

spike duplicate, matrix spike blank) correspond to each batch extracted, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) final volumes and vial identification numbers.

1.7 Inorganic Data

Sample data shall be submitted with the Inorganic Analysis Data Reporting Forms for all samples in the SDG, arranged in increasing alphanumeric DEC sample number order, followed by the QC analyses data, Quarterly Verification of Instrument Parameters forms, raw data, and copies of the digestion and distillation logs.

1.7.1 Results -- Inorganic Analysis Data Sheet (FORM I-CLP-IN)

Tabulated analytical results (identification and quantitation) of the specified analytes (Exhibit C). The validation and release of these results is authorized by a specific, signed statement on the Cover Page. If the Laboratory Manager cannot validate all data reported for each sample, he/she must provide a detailed description of the problems associated with the sample(s) on the Cover Page.

Appropriate concentration units must be specified and entered on Form I-CLP-IN. The quantitative values shall be reported in units of micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. No other units are acceptable. Results for solid sample must be reported on a dry weight basis. Analytical results must be reported to two significant figures if the result value is less than 10; to three significant figures if the value is greater than or equal to 10. Results for percent solids must be reported to one decimal place.

1.7.2 Quality Control Data

1.7.2.1 Initial and Continuing Calibration Verification [FORM II-CLP-IN (Part 1)]

1.7.2.2 CRDL Standard for AA and Linear Range Analysis for ICP [FORM II-CLP-IN (PART 2)]

1.7.2.3 Blanks [FORM III-CLP-IN]

1.7.2.4 ICP Interference Check Sample [FORM IV-CLP-IN]

1.7.2.5 Spike Sample Recovery [FORM V-CLP-IN (PART 1)]

1.7.2.6 Post Digest Spike Sample Recovery [FORM V-CLP-IN (PART 2)]

1.7.2.7 Duplicates [FORM VI-CLP-IN]

1.7.2.8 Laboratory Control Sample [FORM VII-CLP-IN]

1.7.2.9 Standard Addition Results [FORM VIII-CLP-IN]

1.7.2.10 ICP Serial Dilutions [FORM IX-CLP-IN]

1.7.2.11 Holding Times [FORM X-CLP-IN]

1.7.3 Verification of Instrument Parameters

1.7.3.1 Instrument Detection Limits (Quarterly) [FORM XI-CLP-IN]

1.7.3.2 ICP Interelement Correction Factors (Annually) [FORM XII-CLP-IN (PART 1)]

1.7.3.3 ICP Interelement Correction Factors (Annually) [FORM XII-CLP-IN (PART 2)]

1.7.3.4 ICP Linear Ranges (Quarterly) [FORM XIII-CLP-IN]

(Note that copies of Verification of Instrument Parameters forms for the current quarter must be submitted with each data package.)

1.7.4 Raw Data

For each reported value, the Laboratory shall include in the data package all raw data from the instrument used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, as well as sample results. This statement does not apply to the Verifications of Instrument Parameters submitted as part of each data package. Raw data must contain all instrument readouts used for the sample results, including those readouts that may fall below the IDL. All AA and ICP instruments must provide a legible hard copy of the direct real-time instrument readout (i.e., stripcharts, printer tapes, etc.). A photocopy of the direct sequential instrument readout must be included. A hardcopy of the instrument's direct instrument readout for cyanide must be included if the instrumentation has the capability.

The order of raw data in the data package shall be: ICP, Flame AA, Furnace AA, Mercury, and Cyanide. All raw data shall include intensities (ICP) and absorbances with concentration units for flame AA, furnace AA, Mercury and Cyanide. All flame and furnace AA data shall be grouped by element.

Raw data must be labeled with DEC sample number and appropriate codes, shown in Table 1 following to unequivocally identify:

1.7.4.1 Calibration standards, including source and prep date.

1.7.4.2 Initial and continuing calibration blanks and preparation blanks.

1.7.4.3 Initial and continuing calibration verification standards, interference check samples, ICP serial dilution samples, CRDL Standard for ICP and AA, Laboratory Control Sample and Post Digestion Spike.

1.7.4.4 Diluted and undiluted samples (by DEC sample number) and all weights, dilutions and volumes used to obtain the reported values. (If the volumes, weights and dilutions are consistent for all samples in a given SDG, a general statement outlining these parameters is sufficient).

1.7.4.5 Duplicates.

1.7.4.6 Spikes (indicating standard solutions used, final spike concentrations, volumes involved). If spike information (source,

concentration, volume) is consistent for a given SDG, a general statement outlining these parameters is sufficient.

1.7.4.7 Instrument used, any instrument adjustments, data corrections or other apparent anomalies on the measurement record, including all data voided or data not used to obtain reported values and a brief written explanation.

1.7.4.8 All information for furnace analysis clearly and sequentially identified on the raw data, including DEC sample number, sample and analytical spike data, percent recovery, coefficient of variation, full MSA data, MSA correlation coefficient, full MSA data, MSA correlation coefficient, slope and intercepts of linear fit, final sample concentration (standard addition concentration), and type of background correction used: BS for Smith-Heiftje, BD for deuterium Arc, or BZ for Zeeman.

1.7.4.9 Time and date of each analysis. Instrument run logs can be submitted if they contain this information. If the instrument does not automatically provide times of analysis, these must be manually entered on all raw data for initial and continuing calibration verification and blanks, as well as interference check samples and linear range analysis.

1.7.4.10 Integration times for AA analyses.

1.7.5 Copy of Calculations

The Laboratory must provide a copy of the calculations work sheet showing how final results are obtained from values printed on the instrument output report. If manipulations are performed by a software package, a copy of the formula used must be supplied as well as values for all terms in the formula.

1.7.6 Digestion Logs

Logs shall be submitted in the following order: digestion logs for ICP, flame AA, furnace AA and mercury preparations, followed by a copy of the distillation log for cyanide. These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. laboratory control sample, preparation blank) correspond to each batch digested, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) indication of pH <2 or >12, as applicable.

2.0 ASP Category A

2.1 SDG Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: Laboratory name; SDG number; Sample Delivery Group number (SDG); sample numbers in the SDG, differentiating between initial analyses and re-analyses; Contract number; and detailed documentation of any quality control, sample, shipment and/or analytical problems encountered in processing the samples reported in the data package.

Whenever data from sample re-analysis are submitted, the Laboratory shall state in the SDG Narrative for <u>each</u> re-analysis, whether it considers the re-analysis to be billable, and if so, why.

The Laboratory must also include any problems encountered: both technical and administrative, corrective actions taken, and resolution and explanation for all flagged edits (i.e., manual edits) on quantitation lists.

The SDG Narrative shall contain the following statement, verbatim: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on floppy diskette has been authorized by the Laboratory Manager or his designee, as verified by the following signature." This statement shall be directly followed by signature of the Laboratory Manager or his designee with a typed line below it containing the signer's name and title, and the date of signature.

Additionally, the SDG Narrative itself must be signed in original signature by the Laboratory Manager or his designee and dated.

2.2 Contract Lab Sample Information Sheets

A copy of the Contract Lab Sample Information Sheets (CLSIS) for all of the samples in the SDG. The CLSIS shall be arranged in increasing DEC sample number order, considering both letters and numbering in ordering samples.

2.3 NYSDEC Data Package Summary Forms

2.4 Chain-of-Custody Forms

Copies of both the external and internal chain-of-custody sheets for all samples within the SDG.

2.5 GC/MS Volatiles Data

2.5.1 Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet. These sample packets should then be placed in increasing DEC sample number order, considering both letters and numbers in ordering samples.

2.5.1.1 TCL Results - Organic Analysis Data Sheet.

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the SDG Narrative (reference C.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

On Form I, the appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable.

***NOTE**: Report analytical results to one significant figure if the value is less than 10; to two significant figures above 10.*

2.5.1.2 Tentatively Identified Compounds (Form 1-TIC).

This form must be included even if no compounds are found. If so, indicate this on the form by entering "0" in the field for "Number found".

Form I-TIC is the tabulated list of the highest probable match for up to 10 of the non-surrogate organic compounds not listed in Exhibit C for the appropriate program under which the samples were submitted, including the CAS (Chemical Abstracts Registry) number, tentative identification and estimated concentrations. For estimating concentration, assume a response factor of 1, and estimate the concentration by comparison of the compound peak height or total area count to the peak height or total area count of the nearest internal standard free of interferences on the reconstructed ion chromatogram.

***NOTE**: The Laboratory must be consistent, i.e., use peak height for all comparisons or use total area count for all comparisons.*

2.6 GC/MS Semivolatiles Data

2.6.1 Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I, including Form I-TIC). These sample packets should then be placed in increasing DEC sample number order, considering both letters and numbers in ordering samples.

2.6.1.1 TCL Results - Organic Analysis Data Sheet (Form I-SV-1, SV-2).

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the SDG Narrative (Paragraph 2.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

The appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable.

***NOTE**: Report analytical results to one significant figure if the value is less than 10; to two significant figures above 10.*

2.6.1.2 Tentatively Identified Compounds (Form I-TIC)

This form must be included even if no compounds are found. If so, indicate this on the form by entering "0" in the field for "Number found".

Form I-TIC is the tabulated list of the highest probable match for up to 10 of the nonsurrogate organic compounds not listed in Exhibit C, including the CAS (Chemical Abstracts Registry) number, tentative identification and estimated concentration. For estimating concentration, assume a response factor of 1, and estimate the concentration by comparison of the compound peak height or total area count to the peak height or total area count of the

nearest internal standard free of interferences on the reconstructed ion chromatogram.

***NOTE**: The Laboratory must be consistent (i.e., use peak height for all comparisons or use total area count for all comparisons).*

2.7 Pesticide/PCB Data

2.7.1 Sample Data

Sample data shall be arranged in packets with the Traffic Report copy, the Organic Analysis Data Sheet (Form I-PEST). The sample packets should then be placed in increasing DEC sample number order, considering both letters and numbers in ordering samples.

2.7.1.1 Superfund-TCL Results - Organic Analysis Data Sheet (Form I-PEST).

Tabulated results (identification and quantitation) of the specified Superfund target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the SDG Narrative (reference 3.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

The appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable.

***NOTE**: Report analytical results to two significant figures for all pesticide/PCB samples.*

2.8 GC Organic Data

2.8.1 Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet. These sample packets should then be placed in increasing DEC sample number order, considering both letters and numbers in ordering samples.

2.8.1.1 TCL Results - Organic Analysis Data Sheet.

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific signed statement in the SDG Narrative (Paragraph 2.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

The appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable. **NOTE**: Report analytical results to one significant figure if value is less than 10; two significant figures above 10.

2.9 Inorganic Data

Sample data shall be submitted with the Inorganic Analysis Data Reporting Forms for all samples in the SDG, arranged in increasing alphanumeric DEC sample number order.

2.9.1 Results -- Inorganic Analysis Data Sheet (FORM I-IN)

Tabulated analytical results (identification and quantitation) of the specified analytes (Exhibit C). The validation and release of these results is authorized by a specific, signed statement on the Cover Page. If the Laboratory Manager cannot validate all data reported for each sample, he/she must provide a detailed description of the problems associated with the sample(s) on the Cover Page.

Appropriate concentration units must be specified and entered on Form I-CLP-IN. The quantitative values shall be reported in units of micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. No other units are acceptable. Results for solid sample must be reported on a dry weight basis. Analytical results must be reported to two significant figures if the result value is less than 10; to three significant figures if the value is greater than or equal to 10. Results for percent solids must be reported to one decimal place.

2.10 Toxicity Characteristic Leaching Procedure (TCLP) Data

Sample data shall be submitted with the Toxicity Characteristic Leaching Procedure Analysis Data Reporting Forms for all samples in the SDG, arranged in increasing alphanumeric DEC sample number order.

2.10.1 Results -- Toxicity Characteristic Leaching Procedure Analysis Data Sheet (FORM I-TCLP)

Tabulated analytical results (identification and quantitation) of the specified analytes (Exhibit C). The validation and release of these results is authorized by a specific, signed statement on the Cover Page. If the Laboratory Manager cannot validate all data reported for each sample, he/she must provide a detailed description of the problems associated with the sample(s) on the Cover Page.

Appropriate concentration units must be specified and entered on Form I-TCLP. The quantitative values shall be reported in units of micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. No other units are acceptable. Results for solid sample must be reported on a dry weight basis. Analytical results must be reported to two significant figures if the result value is less than 10; to three significant figures if the value is greater than or equal to 10. Results for percent solids must be reported to one decimal place.

3.0 ASP Category B

3.1 SDG Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: Laboratory name; Case number; Sample Delivery Group number (SDG); sample numbers in the SDG, differentiating between initial analyses and re-analyses; Contract number; and detailed documentation of any quality control, sample, shipment and/or analytical problems encountered in processing the samples reported in the data package.

Whenever data from sample re-analysis are submitted, the Laboratory shall state in the SDG Narrative for each re-analysis, whether it considers the re-analysis to be billable, and if so, why.

The Laboratory must also include any problems encountered: both technical and administrative, corrective actions taken, and resolution and an explanation for all flagged edits (i.e., manual edits on quantitation lists.

The SDG Narrative shall contain the following statement, verbatim: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on floppy diskette has been authorized by the Laboratory Manager or his designee, as verified by the following signature." This statement shall be directly followed by signature of the Laboratory Manager or his designee with a typed line below it containing the signer's name and title, and the date of signature.

Additionally, the SDG Narrative itself must be signed in original signature by the Laboratory Manager or his designee and dated.

3.2 Contract Lab Sample Information Sheets

A copy of the Contract Lab Sample Information Sheets (CLSIS) for all of the samples in the SDG. The CLSIS shall be arranged in increasing NYSDEC sample number order, considering both letters and numbering in ordering samples.

3.3 NYSDEC Data Package Summary Forms

3.4 Chain-of-Custody Forms

Copies of both the external and internal chain-of-custody sheets for all samples within the SDG.

3.5 GC/MS Volatiles Data

3.5.1 QC Summary

3.5.1.1 System Monitoring Compound Summary

3.5.1.2 Matrix Spike/Matrix Spike Duplicate Summary

3.5.1.3 QC Check Sample/Standard

3.5.1.4 Method Blank Summary

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank, by instrument.)

3.5.1.5 GC/MS Instrument Performance Check

BFB in chronological order; by instrument.

3.5.1.6 Instrument Detection Limits

3.5.2 Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I-VOA, including Form I-VOA-TIC), followed by the raw data for volatile samples. These sample packets should then be placed in increasing DEC sample number order, considering both letters and numbers in ordering samples.

3.5.2.1 TCL Results - Organic Analysis Data Sheet (Form I-VOA).

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the SDG Narrative (Paragraph 3.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

On Form I-VOA, the appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable.

***NOTE**: Report analytical results to one significant figure if the value is less than 10; to two significant figures above 10.*

3.5.2.2 Tentatively Identified Compounds (Form I-VOA-TIC).

This form must be included even if no compounds are found. If so, indicate this on the form by entering "0" in the field for "Number found".

Form I-VOA-TIC is the tabulated list of the highest probable match for up to 10 organic compounds not system monitoring compounds and not listed in Exhibit C for the appropriate program under which the samples were submitted, including the CAS (Chemical Abstracts Registry) number, tentative identification and estimated concentrations. For estimating concentration, assume a response factor of 1, and estimate the concentration by comparison of the compound peak height or total area count to the peak height or total area count of the nearest internal standard free of interferences on the reconstructed ion chromatogram.

***NOTE**: The Laboratory must be consistent, i.e., use peak height for all comparisons or use total area count for all comparisons.*

3.5.2.3 Reconstructed Total Ion Chromatograms (RIC) for each sample or sample extract.

RICs must be normalized to the largest non-solvent component and contain the following header information:

- NYSDEC sample number
- Date and time of analysis
- GC/MS instrument ID

- Lab file ID

Internal standard and system monitoring compounds are to be labeled with the names of compounds, either directly out from the peak, or on a print-out of retention times if retention times are printed over the peak. If automated system procedures are used for preliminary identification and/or quantification of the target compounds, the complete data system report must be included in all sample data packages in addition to the reconstructed ion chromatogram. The complete data system report shall include all of the information listed below. For laboratories which do not use the automated data system procedures, a laboratory "raw data sheet", which contains the following information, must be included in the sample data package in addition to the chromatogram.

- NYSDEC sample number
- Date and time of analysis
- RT or scan number of identified compounds
- Ion used for quantitation with measured area
- Copy of area table from data system
- GC/MS instrument ID
- Lab file ID

In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report.

3.5.2.4 For each sample, by each compound identified, the following shall be included in the data package:

3.5.2.4.1 Copies of raw spectra and copies of background-subtracted mass spectra of target compounds listed in Exhibit C that are identified in the sample and corresponding background-subtracted TCL standard mass spectra. Spectra must be labeled with NYSDEC sample number, lab file ID, date and time of analysis, and GC/MS instrument ID; compound names must be clearly marked on all spectra.

3.5.2.4.2 Copies of mass spectra of organic compounds not listed in Exhibit C (Tentatively Identified Compounds) with associated best-match spectra (three best matches), labeled as in 3.5.2.4.1 above.

3.5.3 Standards Data

3.5.3.1 Initial Calibration Data (Form IV-VOA) - in order by instrument if more than one instrument used.

3.5.3.1.1 VOA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for the initial calibration, labeled as in 3.5.2.3 above. Spectra are not required.

3.5.3.1.2 All initial calibration data that pertain to samples in the data package must be included, regardless of when it was performed and for which case. When more than one initial calibration is performed, the data must be put in chronological order, by instrument.

3.5.3.2 Continuing Calibration (Form VII-VOA) - in order by instrument, if more than one instrument used.

3.5.3.2.1 VOA standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for all continuing (12 hour) calibrations, labeled as in 3.5.2.3. Spectra are not required.

3.5.3.2.2 When more than one continuing calibration is performed, forms must be in chronological order, within fraction and instrument.

3.5.4 Raw QC Data

3.5.4.1 BFB (for each 12-hour period, for each GC/MS system utilized)

3.5.4.1.1 Bar graph spectrum, labeled as in 3.5.2.3.

3.5.4.1.2 Mass listing, labeled as in 3.5.2.3.

3.5.4.1.3 Reconstructed total ion chromatogram (RIC), labeled as in 3.5.2.3.

3.5.4.2 Blank Data - in chronological order.

***NOTE**: This order is different from that used for samples.*

3.5.4.2.1 Tabulated results (Form I-VOA)

3.5.4.2.2 Tentatively Identified Compounds (Form I-VOA-TIC) - even if none found.

3.5.4.2.3 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.4.2.3.

3.5.4.2.4 TCL spectra with lab generated standard, labeled as in 3.5.2.4. Data systems which are incapable of dual display shall provide spectra in the following order:

- Raw TCL compound spectra
- Enhanced or background subtracted spectra

- Laboratory generated TCL standard spectra

3.5.4.2.5 GC/MS library search spectra for Tentatively Identified Compounds (TIC), labeled as in 3.5.2.4.

3.5.4.2.6 Quantitation/Calculation of Tentatively Identified Compound(s) (TIC) concentrations

3.5.4.3 Matrix Spike Blank Data

3.5.4.3.1 Tabulated results (Form I-VOA) of all TCL compounds. Form I-VOA-TIC is not required.

3.5.4.3.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.5.2.4. Spectra are not required.

3.5.4.4 Matrix Spike Data

3.5.4.4.1 Tabulated results (Form I-VOA) of all TCL compounds. Form I-VOA-TIC is not required.

3.5.4.4.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.5.2.4. Spectra are not required.

3.5.4.5 Matrix Spike Duplicate Data

3.5.4.5.1 Tabulated results (Form I-VOA) of all TCL Compounds. Form I-VOA-TIC is not required.

3.5.4.5.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.5.2.4. Spectra are not required.

3.5.4.6 QC Check Sample/Standard

3.5.4.6.1 Tabulated results (Form I-VOA) of all TCL Compounds. Form I-VOA-TIC is not required.

3.5.4.6.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.5.2.4. Spectra are not required.

3.5.5 Copy of Calculations

The Laboratory must provide a copy of the calculations work sheet showing how final results are obtained from values printed on the quantitation report. If manipulations are performed by a software package, a copy of the formula used must be supplied as well as values for all terms in the formula.

3.5.6 Copy of Extraction Logs

These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. matrix spike, matrix spike duplicate, matrix spike blank) correspond to each batch extracted, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) final volumes and vial identification numbers.

3.6 GC/MS Semivolatiles Data

3.6.1 QC summary

3.6.1.1 Surrogate Percent Recovery Summary (Form II-SV)

3.6.1.2 Matrix Spike/Matrix Spike Duplicate Summary (Form III-SV)

3.6.1.3 QC Check Sample/Standard

3.6.1.4 Method Blank Summary (Form IV-SV)

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank.)

3.6.1.5 GC/MS Instrument Performance and Mass Calibration (Form V-SV)

DFTPP in chronological order; by instrument.

3.6.1.6 Internal Standard Area and RT Summary (Form VIII-SV)

3.6.1.7 Instrument Detection Limits

3.6.2 Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I-CLP-SV, including Form I SV-TIC), followed by the raw data for semivolatile samples. These sample packets should then be placed in increasing DEC sample number order, considering both letters and numbers in ordering samples.

3.6.2.1 TCL Results - Organic Analysis Data Sheet (Form I-SV-1, SV-2).

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the SDG Narrative (Paragraph 3.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

On Form I-SV, the appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable.

***NOTE**: Report analytical results to one significant figure if the value is less than 10; to two significant figures above 10.*

3.6.2.2 Tentatively Identified Compounds (Form I-SV-TIC)

This form must be included even if no compounds are found. If so, indicate this on the form by entering "0" in the field for "Number found".

Form I-SV-TIC is the tabulated list of the highest probable match for up to 20 of the nonsurrogate organic compounds not listed in Exhibit C, including the CAS (Chemical Abstracts Registry) number, tentative identification and estimated concentration. For estimating concentration, assume a response factor of 1, and estimate the concentration by comparison of the compound peak height or total area count to the peak height or total area count of the nearest internal standard free of interferences on the reconstructed ion chromatogram.

***NOTE**: The Laboratory must be consistent (i.e., use peak height for all comparisons or use total area count for all comparisons).*

3.6.2.3 Reconstructed total ion chromatograms (RIC) for each sample, sample extract, standard, blank, and spiked sample.

RICs must be normalized to the largest nonsolvent component, and must contain the following header information:

- NYSDEC sample number
- Date and time of analysis
- GC/MS instrument ID
- Lab file ID

In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initialing and dating the changes made to the report.

Internal standard and surrogate spiking compounds are to be labeled with the names of compounds, either directly out from the peak, or on a print-out of retention times if retention times are printed over the peak. If automated data system procedures are used for preliminary identification and/or quantification of the Target Compound List compounds, the complete data system report must be included in all sample data packages, in addition to the reconstructed ion chromatogram. The complete data system report shall include all of the information listed below. For laboratories which do not use the automated data system procedures, a laboratory "raw data sheet," containing the following information, must be included in the sample data package in addition to the chromatogram.

- NYSDEC sample number
- Date and time of analysis

- RT or scan number of identified TCL compounds
- Ion used for quantitation with measured area
- Copy of area table from data system
- GC/MS instrument ID
- Lab file ID

3.6.2.4 For each sample, by each compound identified, the following shall be included in the data package:

3.6.2.4.1 Copies of raw spectra and copies of background-subtracted mass spectra of target compounds listed in Exhibit C that are identified in the sample and corresponding background-subtracted TCL standard mass spectra. Spectra must be labeled with NYSDEC sample number, lab file ID, date and time of analysis, and GC/MS instrument ID; compound names must be clearly marked on all spectra.

3.6.2.4.2 Copies of mass spectra of nonsurrogate organic compounds not listed in Exhibit C (Tentatively Identified Compounds) with associated best-match spectra (three best matches), labeled as in 3.6.2.3.

3.6.2.4.3 GPC chromatograms (if GPC performed).

3.6.3 Standards Data

3.6.3.1 Initial Calibration Data (Form VI-SV-1, SV-2) - in order by instrument, if more than one instrument used.

3.6.3.1.1 Semivolatile standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for the initial calibration, labeled in 3.6.2.3. Spectra are <u>not</u> required.

3.6.3.1.2 All initial calibration data that pertain to samples in the data package must be included, regardless of when it was performed and for which SDG. When more than one initial calibration is performed, the data must be put in chronological order, by instrument.

3.6.3.2 Continuing calibration (Form VII-SV-1, SV-2) - in order by instrument, if more than one instrument used.

3.6.3.2.1 Semivolatile standard(s) reconstructed ion chromatograms and quantitation reports (or legible facsimile) for all continuing (12 hour) calibrations, labeled as in 3.6.2.3. Spectra are <u>not</u> required.

3.6.3.2.2 When more than one continuing calibration is performed, forms must be in chronological order, by instrument.

3.6.3.3 Internal Standard Area Summary (Form VIII-SV-1, SV-2) in order by instrument, if more than one instrument used.

When more than one continuing calibration is performed, forms must be in chronological order by instrument.

3.6.3.4 Semivolatile GPC Calibration Data - UV detector traces showing peaks that correspond to the compounds in the semivolatile GPC calibration mixture. Traces must be labeled with GPC column identifier, date of calibration, and with compound names labeled either directly out from the peak, or on a printout of retention times, if retention times are printed over the peak. Do not include Form IX Pest-2, as the compounds used on that form are not appropriate for semivolatile sample extracts.

3.6.4 Raw QC Data

3.6.4.1 DFTPP (for each 12-hour period, for each GC/MS system utilized)

3.6.4.1.1 Bar graph spectrum, labeled as in 3.6.2.3.

3.6.4.1.2 Mass listing, labeled as in 3.6.2.3.

3.6.4.1.3 Reconstructed total ion chromatogram (RIC), labeled as in 3.6.2.3.

3.6.4.2 Blank Data - in chronological order, by extraction date.
NOTE: This order is different from that used for samples.

3.6.4.2.1 Tabulated results (Form I-SV-1, SV-2)

3.6.4.2.2 Tentatively Identified Compounds (Form I-SV-TIC) - even if none found.

3.6.4.2.3 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.6.2.3.

3.6.4.2.4 Superfund-TCL spectra with lab generated standard, labeled as in 3.6.2.4. Data systems which are incapable of dual display shall provide spectra in order:

- Raw TCL compound spectra
- Enhanced or background subtracted spectra
- Laboratory generated TCL standard spectra

3.6.4.2.5 GC/MS library search spectra for Tentatively Identified Compounds (TIC), labeled as in 3.6.2.4.

3.6.4.2.6 Quantitation/Calculation of Tentatively Identified Compound(s) (TIC) concentrations

3.6.4.3 Matrix Spike Blank Data

3.6.4.3.1 Tabulated results (Form I-SV-1, SV-2) of all TCL compounds. Form I-SV-TIC not required.

3.6.4.3.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.6.2.3. Spectra are required.

3.6.4.4 Matrix Spike Data

3.6.4.4.1 Tabulated results (Form I-SV-1, SV-2) of all TCL compounds. Form I-SV-TIC not required.

3.6.4.4.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.6.2.3. Spectra are not required.

3.6.4.5 Matrix Spike Duplicate Data

3.6.4.5.1 Tabulated results (Form I-SV-1, SV-2) of all TCL compounds. Form I-SV-TIC not required.

3.6.4.5.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.6.2.3. Spectra are not required.

3.6.4.6 QC Check Sample/Standard

3.6.4.6.1 Tabulated results (Form I-SV-1,SV-2) of all TCL compounds.

3.6.4.6.2 Reconstructed ion chromatogram(s) and quantitation report(s) or legible facsimile (GC/MS), labeled as in 3.6.2.3. Spectra are not required.

3.6.5 Copy of Calculations

The Laboratory must provide a copy of the calculations work sheet showing how final results are obtained from values printed on the quantitation report. If manipulations are performed by a software package, a copy of the formula used must be supplied as well as values for all terms in the formula.

3.6.6 Copy of Extraction Logs

These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. matrix spike, matrix spike duplicate, matrix spike blank) correspond to each batch extracted, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) final volumes and vial identification numbers.

3.7 GC/ECD Pesticide/Aroclor Data

3.7.1 QC Summary

3.7.1.1 Surrogate Percent Recovery Summary (Form II-PEST)

3.7.1.2 Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Summary (Form III-PEST)

3.7.1.3 QC Check Sample/Standard Recovery

3.7.1.4 Method Blank Summary (Form IV-PEST)

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank.)

3.7.1.5 Instrument Detection Limits

3.7.2 Sample Data

Sample data shall be arranged in packets with the Traffic Report copy, the Organic Analysis Data Sheet (Form I-PEST), followed by the raw data for pesticide samples. The sample packets should then be placed in increasing NYSDEC sample number order, considering both letters and numbers in ordering samples.

3.7.2.1 TCL Results - Organic Analysis Data Sheet (Form I-PEST).

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific, signed statement in the SDG Narrative (Paragraph 3.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

On Form I-PEST, the appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable.

NOTE: Report analytical results to two significant figures for all pesticide/PCB samples.

3.7.2.2 Copies of pesticide chromatograms.

All chromatograms must be labeled with the following information.

- NYSDEC sample number
- Volume injected (µl)
- Date and time of injection
- GC column identification (by stationary phase and internal diameter)
- GC instrument identification
- Positively identified compounds must be labeled with the names of compounds, either directly out from the peak, or on a print-

out of retention times if retention times are printed over the peak.

3.7.2.3 Copies of pesticide chromatograms from second GC column confirmation. Chromatograms to be labeled as in 3.7.2.2 above.

3.7.2.4 GC integration report or data system printout and calibration plots (area vs. concentration) for 4-4'-DDT, 4,4'-DDD, 4,4'-DDE or toxaphene (where appropriate).

3.7.2.5 Manual work sheets.

3.7.2.6 UV traces from GPC (if GPC performed).

3.7.2.7 If pesticide/Aroclors are confirmed by GC/MS, the Laboratory shall submit copies of reconstructed ion chromatograms, raw spectra and copies of background-subtracted mass spectra of Superfund target compounds listed in Exhibit C (Superfund-TCL) that are identified in the sample and corresponding background-subtracted Superfund-TCL standard mass spectra. Compound names must be clearly marked on all spectra. For multicomponent pesticides/Aroclors confirmed by GC/MS, the Laboratory shall submit mass spectra of 3 major peaks of multicomponent compounds from samples and standards.

3.7.3 Standards Data

3.7.3.1 Initial Calibration of Single Component Analytes (Form VI-PEST-1 and PEST-2) - all GC columns, all instruments, in chronological order by GC column and instrument.

3.7.3.2 Initial Calibration of Multicomponent Analytes (Form VI-PEST-3) - all GC columns, all instruments, in chronological order by GC column and instrument

3.7.3.3 Analyte Resolution Summary (Form VI-PEST-4) - all GC columns and instruments, in chronological order by GC column and instrument.

3.7.3.4 Calibration Verification Summary (Form VII-PEST-1) - for all Performance Evaluation Mixtures and Instrument blanks, on all GC columns and instruments, in chronological order by GC column and instrument.

3.7.3.5 Calibration Verification Summary (Form VII-PEST-2) - for all mid point concentrations of Individual Standard Mixtures A and B and Instrument blanks used for calibration verification, on all GC columns and instruments, in chronological order by GC column and instrument.

3.7.3.6 Analytical Sequence (Form VIII-PEST) - all GC columns and instruments, in chronological order by GC column and instrument.

3.7.3.7 Florisil Cartridge Check (Form IX-PEST-1) - for all lots of cartridges used to process samples in the SDG.

3.7.3.8 Pesticide GPC Calibration (Form IX-PEST-2) - all GPC columns, in chronological order by calibration date.

3.7.3.9 Pesticide Identification Summary for Single Component Analytes (Form X-PEST-1) - for all samples with positively identified single component analytes, in order by increasing NYSDEC sample number.

3.7.3.10 Pesticide Identification Summary for Multicomponent Analytes (Form X-PEST-2) - for all samples with positively identified multicomponent analytes, in order by increasing NYSDEC sample number.

3.7.3.11 Chromatograms and data system printouts are required for all standards including the following:

- Resolution Check Mixture.
- Performance Evaluation Mixtures, all.
- Individual Standard Mixture A, at three concentrations, each initial calibration.
- Individual Standard Mixture B, at three concentrations, each initial calibration.
- All multicomponent analytes (Toxaphene and Aroclors), each initial calibration.
- All mid point concentrations of Individual Standard Mixtures A and B used for calibration verification.
- Florisil cartridge check solution, all lots.
- Pesticide GPC Calibration Check Solution, all calibrations relating to samples in the SDG.
- All multicomponent analyte standards analyzed for confirmation.

3.7.3.12 A printout of retention times and corresponding peak areas or peak heights must accompany each chromatogram. In addition, all chromatograms are required to be labeled with the following:

- NYSDEC Sample Number for the standard, i.e., INDA1, INDA2, etc. (See Forms Instructions for details).
- Label all standard peaks for all individual compounds either directly out from the peak or on the printout of retention times if retention times are printed over the peak.
- Total nanograms injected for each standard.
- Date and time of injection.
- GC column identification (by stationary phase and internal diameter).

- GC instrument identification.

3.7.3.13 Pesticide GPC Calibration Data - UV detector traces showing peaks that correspond to the compounds in the pesticide GPC calibration mixture. Traces must be labeled with GPC column identifier, date of calibration, and with compound names labeled either directly out from the peak, or on a printout of retention times, if retention times are printed over the peak.

3.7.4 Raw QC Data

3.7.4.1 Blank Data - in chronological order, by type of blank (method, instrument, sulfur cleanup).

***NOTE**: This order is different from that used for samples.*

3.7.4.1.1 Tabulated results (Form I-PEST).

3.7.4.1.2 Chromatogram(s) and data system printout(s) (GC) for each GC column and instrument used for analysis, labeled as in 3.7.2.2 above.

3.7.4.2 Matrix Spike Data

3.7.4.2.1 Tabulated results (Form I-PEST) of <u>all</u> TCL compounds.

3.7.4.2.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 3.7.2.2 above.

3.7.4.3 Matrix Spike Duplicate Data

3.7.4.3.1 Tabulated results (Form I-PEST) of <u>all</u> TCL compounds.

3.7.4.3.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 3.7.2.2 above

3.7.4.4 Matrix Spike Blank Data

3.7.4.4.1 Tabulated results (Form I-PEST) of <u>all</u> TCL compounds.

3.7.4.4.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 3.7.2.2 above

3.7.4.5 QC Check Sample/Standard

3.7.4.5.1 Tabulated results (Form I-PEST) of <u>all</u> TCL compounds.

3.7.4.5.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 3.7.2.2 above.

3.6.5 Copy of Calculations

The Laboratory must provide a copy of the calculations work sheet showing how final results are obtained from values printed on the quantitation report. If manipulations are performed by a software package, a copy of the formula used must be supplied as well as values for all terms in the formula.

3.6.6 Copy of Extraction Log

These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. matrix spike, matrix spike duplicate, matrix spike blank) correspond to each batch extracted, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) final volumes and vial identification numbers.

3.8 GC Organic Data

3.8.1 QC Summary

3.8.1.1 Surrogate Percent Recovery Summary (Form II-GC)

3.8.1.2 Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Summary (Form III-GC)

3.8.1.3 QC Check Sample/Standard

3.8.1.3.1 Tabulated results (Form I-PEST) of <u>all</u> TCL compounds.

3.8.1.3.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 3.8.2.2.

3.8.1.4 Method Blank Summary (Form IV-GC)

(If more than a single form is necessary, forms must be arranged in chronological order by date of analysis of the blank.)

3.8.1.5 Instrument Detection Limits

3.8.2 Sample Data

Sample data shall be arranged in packets with the Organic Analysis Data Sheet (Form I GC), followed by the raw data for pesticide samples. These sample packets should then be placed in increasing NYSDEC sample number order, considering both letters and numbers in ordering samples.

3.8.2.1 TCL Results - Organic Analysis Data Sheet (Form I-GC).

Tabulated results (identification and quantitation) of the specified target compounds (Exhibit C). The validation and release of these results is authorized by a specific signed statement in the SDG Narrative (Paragraph 3.1). In the event that the Laboratory Manager cannot validate all data reported for each sample, the Laboratory Manager shall provide a detailed description of the problems associated with the sample in the SDG Narrative.

On Form I-GC, the appropriate concentration units shall be entered. For example, µg/L for water samples or µg/Kg for soil/sediment samples. No other units are acceptable.

***NOTE**: Report analytical results to one significant figure if value is less than 10; two significant figures above 10.*

3.8.2.2 Copies of chromatograms.

All chromatograms must be labeled with the following information:

- NYSDEC sample number
- Volume injected (µL)
- Date and time of injection
- GC column identification (by stationary phase)
- GC instrument identification
- Positively identified compounds must be labeled with the names of compounds, either directly out from the peak, or on a print-out of retention times if retention times are printed over the peak.

3.8.2.3 Copies of chromatograms from second GC column confirmation. Chromatograms to be labeled as in 3.8.2.2.

3.8.2.4 GC integration report or data system printout and calibration plots (area vs. concentration) (where appropriate).

3.8.2.5 Manual work sheets.

3.8.2.6 GPC chromatograms (if GPC performed).

3.8.3 Standards Data

3.8.3.1 Initial Calibration Data

3.8.3.2 Continuing Calibration Data

3.8.3.3 QC Check Sample/Standard (as required per method)

3.8.3.4 Standard chromatograms and data system printouts for <u>all</u> standards.

3.8.3.4.1 All chromatograms are required to have the following:

- Label all standard peaks for all individual compounds either directly out from the peak or on the printout of retention times if retention times are printed over the peak.

- Label the chromatogram for multicomponent standards.
- List total ng injected for each standard.
- A printout of retention times and corresponding peak areas must accompany each chromatogram.
- Date and time of injection.
- GC column identification (by stationary phase).
- GC instrument identification.

3.8.4 Raw QC Data

3.8.4.1 Blank Data - in chronological order.

***NOTE**: This order is different from that used for samples.*

3.8.4.1.1 Tabulated results.

3.8.4.1.2 Chromatogram(s) and data system printout(s) (GC) for each GC column and instrument used for analysis.

3.8.4.2 Matrix Spike Data

3.8.4.2.1 Tabulated results of all TCL compounds.

3.8.4.2.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 3.8.2.2.

3.8.4.3 Matrix Spike Duplicate Data

3.8.4.3.1 Tabulated results of all TCL compounds.

3.8.4.3.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 3.8.2.2.

3.8.4.4 QC Check Sample/Standard

3.8.4.4.1 Tabulated results of all TCL compounds.

3.8.4.4.2 Chromatogram(s) and data system printout(s) (GC), labeled as in 3.8.2.2.

3.8.5 Copy of Calculations

The Laboratory must provide a copy of the calculations work sheet showing how final results are obtained from values printed on the quantitation report. If manipulations are performed by a software package, a copy of the formula used must be supplied as well as values for all terms in the formula.

3.8.6 Copy of Extraction Log

These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. matrix spike, matrix spike duplicate, matrix spike blank) correspond to each batch extracted, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) final volumes and vial identification numbers.

3.9 Inorganic Data

Sample data shall be submitted with the Inorganic Analysis Data Reporting Forms for all samples in the SDG, arranged in increasing alphanumeric DEC sample number order, followed by the QC analyses data, Quarterly Verification of Instrument Parameters forms, raw data, and copies of the digestion and distillation logs.

3.9.1 Results -- Inorganic Analysis Data Sheet (Form I-IN)

Tabulated analytical results (identification and quantitation) of the specified analytes (Exhibit C). The validation and release of these results is authorized by a specific, signed statement on the Cover Page. If the Laboratory Manager cannot validate all data reported for each sample, he/she must provide a detailed description of the problems associated with the sample(s) on the Cover Page.

Appropriate concentration units must be specified and entered on Form I-IN. The quantitative values shall be reported in units of micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. No other units are acceptable. Results for solid sample must be reported on a dry weight basis. Analytical results must be reported to two significant figures if the result value is less than 10; to three significant figures if the value is greater than or equal to 10. Results for percent solids must be reported to one decimal place.

3.9.2 Quality Control Data

3.9.2.1 Initial and Continuing Calibration Verification [FORM II-IN (Part 1)]

3.9.2.2 CRDL Standard for AA and Linear Range Analysis for ICP [FORM II-IN (PART 2)]

3.9.2.3 Blanks [FORM III-IN]

3.9.2.4 ICP Interference Check Sample [FORM IV-IN]

3.9.2.5 Spike Sample Recovery [FORM V-IN (PART 1)]

3.9.2.6 Post Digest Spike Sample Recovery [FORM V-IN (PART 2)]

3.9.2.7 Duplicates [FORM VI-IN]

3.9.2.8 Quality Control Sample [FORM VII-IN]

3.9.2.9 Standard Addition Results [FORM VIII-IN]

3.9.2.10 ICP Serial Dilutions [FORM IX-IN]

3.9.2.11 Holding Times [FORM X-IN]

3.9.3 Verification of Instrument Parameters

3.9.3.1 Instrument Detection Limits (Semiannually) [FORM XI-IN]

3.9.3.2 ICP Interelement Correction Factors (Annually) [FORM XII-IN (PART 1)]

3.9.3.3 ICP Interelement Correction Factors (Annually) [FORM XII-IN (PART 2)]

3.9.3.4 ICP Linear Ranges (Quarterly) [FORM XIII-IN]

(Note that copies of Verification of Instrument Parameters forms for the current quarter must be submitted with each data package.)

3.9.4 Raw Data

For each reported value, the Laboratory shall include in the data package all raw data from the instrument used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, as well as sample results. This statement does not apply to the Verifications of Instrument Parameters submitted as part of each data package. Raw data must contain all instrument readouts used for the sample results, including those readouts that may fall below the IDL. All AA and ICP instruments must provide a legible hard copy of the direct real-time instrument readout (i.e., stripcharts, printer tapes, etc.). A photocopy of the direct sequential instrument readout must be included. A hardcopy of the instrument's direct instrument readout for cyanide must be included if the instrumentation has the capability.

The order of raw data in the data package shall be: ICP, Flame AA, Furnace AA, Mercury, and Cyanide. All raw data shall include intensities (ICP) and absorbances with concentration units for flame AA, furnace AA, Mercury and Cyanide. All flame and furnace AA data shall be grouped by element.

Raw data must be labeled with NYSDEC sample number and appropriate codes, shown in Table 1 following to unequivocally identify:

3.9.4.1 Calibration standards, including source and prep date.

3.9.4.2 Initial and continuing calibration blanks and preparation blanks.

3.9.4.3 Initial and continuing calibration verification standards, interference check samples, ICP serial dilution samples, CRDL Standard for ICP and AA, Laboratory Control Sample and Post Digestion Spike.

3.9.4.4 Diluted and undiluted samples (by DEC sample number) and all weights, dilutions and volumes used to obtain the reported values. (If the volumes, weights and dilutions are consistent for all samples in a given SDG, a general statement outlining these parameters is sufficient).

3.9.4.5 Duplicates.

3.9.4.6 Spikes (indicating standard solutions used, final spike concentrations, volumes involved). If spike information (source, concentration, volume) is consistent for a given SDG, a general statement outlining these parameters is sufficient.

3.9.4.7 Instrument used, any instrument adjustments, data corrections or other apparent anomalies on the measurement record, including all data voided or data not used to obtain reported values and a brief written explanation.

3.9.4.8 All information for furnace analysis clearly and sequentially identified on the raw data, including NYSDEC sample number, sample and analytical spike data, percent recovery, coefficient of variation, full MSA data, MSA correlation coefficient, full MSA data, MSA correlation coefficient, slope and intercepts of linear fit, final sample concentration (standard addition concentration), and type of background correction used: BS for Smith-Heiftje, BD for deuterium Arc, or BZ for Zeeman.

3.9.4.9 Time and date of each analysis. Instrument run logs can be submitted if they contain this information. If the instrument does not automatically provide times of analysis, these must be manually entered on all raw data for initial and continuing calibration verification and blanks, as well as interference check samples and linear range analysis.

3.9.4.10 Integration times for AA analyses.

3.9.5 Digestion Logs

Logs shall be submitted in the following order: digestion logs for ICP, flame AA, furnace AA and mercury preparations, followed by a copy of the distillation log for cyanide. These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. laboratory control sample, preparation blank) correspond to each batch digested, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) indication of pH <2 or >12, as applicable.

3.10 Wet-Chemical Data

Sample data shall be submitted with the Conventional Analysis Data Reporting Forms for all sample in the SDG, arranged in increasing alphanumeric NYSDEC sample number order, followed by the QC analyses data, Quarterly Verification of Instrument Parameters forms, raw data, and copies of the digestion and distillation logs.

3.10.1 Results -- Wet-Chemical Analysis Data Sheet

Tabulated analytical results (identification and quantitation) of the specified analytes (Exhibit C). The validation and release of these results is authorized by a specific, signed statement on the Cover Page. If the Laboratory Manager cannot validate all data reported for each sample, he/she must provide a detailed description of the problems associated with the sample(s) on the Cover Page.

Appropriate concentration units must be specified and entered on Form I. The quantitative values shall be reported in units of micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. No other units are acceptable. Results for solid samples must be reported on a dry weight basis. Analytical results must be reported to two significant figures if the result value is less than 10; to three significant figures if the value is greater than or equal to 10. Results for percent solids must be reported to one decimal place.

3.10.2 Quality Control Data

3.10.2.1 Initial and Continuing Calibration Verification

3.10.2.2 CRQL Standard for Wet-Chemical Analysis

3.10.2.3 Blanks

3.10.2.4 Spike Sample Recovery

3.10.2.5 Post Digest Spike Sample Recovery

3.10.2.6 Duplicates

3.10.2.7 Laboratory Control Sample

3.10.2.8 Holding Times

3.10.3 Raw Data

For each reported value, the Laboratory shall include in the data package all raw data from the instrument used to obtain that value and the QA/QC values reported (except for raw data for quarterly verifications of instrument parameters). Raw data must contain all instrument readouts used for the sample results, including those readouts that may fall below the IDG. ALL instruments must provide a legible hard copy of the direct real-time instrument readout (i.e., stripcharts, printer tapes, etc.). A photocopy of the direct sequential instrument readout must be included. A hardcopy of the direct instrument readout for cyanide must be included if the instrumentation has the capability. All raw data shall include absorbances with concentration units (unless instrument direct readout is in

concentration units). A photocopy of manual worksheets used must be included for all non-instrumental parameters.

Raw data must be labeled with NYSDEC sample number to unequivocally identify:

3.10.3.1 Calibration standards, including source and prep date.

3.10.3.2 Initial and continuing calibration blanks and preparation blanks.

3.10.3.3 Initial and continuing calibration verification standards.

3.10.3.4 Diluted and undiluted samples (by NYSDEC sample number) and all weights, dilutions and volumes used to obtain the reported values. (If the volumes, weights and dilutions are consistent for all samples in a given SDG, a general statement outlining these parameters is sufficient).

3.10.3.5 Duplicates.

3.10.3.6 Spikes (indicating standard solutions used, final spike concentrations, volumes involved). If spike information (source, concentration, volume) is consistent for a given SDG, a general statement outlining these parameters is sufficient.

3.10.3.7 Instrument used, any instrument adjustments, data corrections or other apparent anomalies on the measurement record, including all data voided or data not used to obtain reported values and a brief written explanation.

3.10.3.8 Time and date of each analysis. Instrument run logs can be submitted if they contain this information. If the instrument does not automatically provide times of analysis, these must be manually entered on all raw data for initial and continuing calibration verification and blanks, as well as interference check samples and linear range analysis.

3.10.4 Digestion and Distillation Logs

These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e., laboratory control sample, preparation blank) correspond to each batch digested, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) indication of pH <2 or >12, as applicable.

3.11 Toxicity Characteristic Leaching Procedure (TCLP) Data

Sample data shall be submitted with the Toxicity Characteristic Leaching Procedure Analysis Data Reporting Forms for all samples in the SDG, arranged in increasing alphanumeric DEC sample number order, followed by the QC analyses data, Quarterly Verification of Instrument Parameters forms, raw data, and copies of the digestion and distillation logs.

3.11.1 Results -- Toxicity Characteristic Leaching Procedure (TCLP) Analysis Data Sheet (Form I-TCLP)

Tabulated analytical results (identification and quantitation) of the specified analytes (Exhibit C). The validation and release of these results is authorized by a specific, signed statement on the Cover Page. If the Laboratory Manager cannot validate all data reported for each sample, he/she must provide a detailed description of the problems associated with the sample(s) on the Cover Page.

Appropriate concentration units must be specified and entered on Form I-IN. The quantitative values shall be reported in units of milligrams per liter (mg/L). No other units are acceptable. Analytical results must be reported to two significant figures if the result value is less than 10; to three significant figures if the value is greater than or equal to 10. Results for percent solids must be reported to one decimal place.

3.11.2 TCLP Inorganic Quality Control Data

3.11.2.1 Initial and Continuing Calibration Verification [FORM II-IN (Part 1)]

3.11.2.2 CRDL Standard for AA and Linear Range Analysis for ICP [FORM II-IN (PART 2)]

3.11.2.3 Blanks [FORM III-IN]

3.11.2.4 ICP Interference Check Sample [FORM IV-IN]

3.11.2.5 Spike Sample Recovery [FORM V-IN (PART 1)]

3.11.2.6 Post Digest Spike Sample Recovery [FORM V-IN (PART 2)]

3.11.2.7 Duplicates [FORM VI-IN]

3.11.2.8 Quality Control Sample [FORM VII-IN]

3.11.2.9 Standard Addition Results [FORM VIII-IN]

3.11.2.10 ICP Serial Dilutions [FORM IX-IN]

3.11.2.11 Holding Times [FORM X-IN]

3.11.3 Verification of Instrument Parameters

3.11.3.1 Instrument Detection Limits (Semiannually) [FORM XI-IN]

3.11.3.2 ICP Interelement Correction Factors (Annually) [FORM XII-IN (PART 1)]

3.11.3.3 ICP Interelement Correction Factors (Annually) [FORM XII-IN (PART 2)]

3.11.3.4 ICP Linear Ranges (Quarterly) [FORM XIII-IN]

NOTE: *Copies of Verification of Instrument Parameters forms for the current quarter must be submitted with each data package.*

3.11.4 Raw Data

For each reported value, the Laboratory shall include in the data package all raw data from the instrument used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, as well as sample results. This statement does not apply to the Verifications of Instrument Parameters submitted as part of each data package. Raw data must contain all instrument readouts used for the sample results, including those readouts that may fall below the IDL. All AA and ICP instruments must provide a legible hard copy of the direct real-time instrument readout (i.e., stripcharts, printer tapes, etc.). A photocopy of the direct sequential instrument readout must be included. A hardcopy of the instrument's direct instrument readout for cyanide must be included if the instrumentation has the capability.

The order of raw data in the data package shall be: ICP, Flame AA, Furnace AA, Mercury, and Cyanide. All raw data shall include intensities (ICP) and absorbances with concentration units for flame AA, furnace AA, Mercury and Cyanide. All flame and furnace AA data shall be grouped by element.

Raw data must be labeled with NYSDEC sample number and appropriate codes, shown in Table 1 following to unequivocally identify:

3.11.4.1 Calibration standards, including source and prep date.

3.11.4.2 Initial and continuing calibration blanks and preparation blanks.

3.11.4.3 Initial and continuing calibration verification standards, interference check samples, ICP serial dilution samples, CRDL Standard for ICP and AA, Laboratory Control Sample and Post Digestion Spike.

3.11.4.4 Diluted and undiluted samples (by DEC sample number) and all weights, dilutions and volumes used to obtain the reported values. (If the volumes, weights and dilutions are consistent for all samples in a given SDG, a general statement outlining these parameters is sufficient).

3.11.4.5 Duplicates.

3.11.4.6 Spikes (indicating standard solutions used, final spike concentrations, volumes involved). If spike information (source, concentration, volume) is consistent for a given SDG, a general statement outlining these parameters is sufficient.

3.11.4.7 Instrument used, any instrument adjustments, data corrections or other apparent anomalies on the measurement record, including all data voided or data not used to obtain reported values and a brief written explanation.

3.11.4.8 All information for furnace analysis clearly and sequentially identified on the raw data, including NYSDEC sample number,

sample and analytical spike data, percent recovery, coefficient of variation, full MSA data, MSA correlation coefficient, full MSA data, MSA correlation coefficient, slope and intercepts of linear fit, final sample concentration (standard addition concentration), and type of background correction used: BS for Smith-Heiftje, BD for deuterium Arc, or BZ for Zeeman.

3.11.4.9 Time and date of each analysis. Instrument run logs can be submitted if they contain this information. If the instrument does not automatically provide times of analysis, these must be manually entered on all raw data for initial and continuing calibration verification and blanks, as well as interference check samples and linear range analysis.

3.11.4.10 Integration times for AA analyses.

3.11.5 Digestion Logs

Logs shall be submitted in the following order: digestion logs for ICP, flame AA, furnace AA and mercury preparations, followed by a copy of the distillation log for cyanide. These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e. laboratory control sample, preparation blank) correspond to each batch digested, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) indication of pH <2 or >12, as applicable.

F. - Data In Computer Readable Form

Exhibit H details the requirements for data in computer-readable form. The specific requirements depend on the reporting category requested (Superfund, A, or B) and the analytical method used.

The Laboratory shall provide a computer-readable copy of the data on data report Forms I-XIV for all samples in the Delivery Group, as specified in the Contract Performance/Delivery Schedule. Computer-readable data deliverables shall be submitted on IBM or IBM-compatible 3.5 inch high density 1.44 M-byte diskette. The data shall be recorded in ASCII, text file format, and shall adhere to the file, record and field specifications listed in Exhibit H, Data Dictionary and Format for Data Deliverables in Computer-Readable Format.

DEC is still in the process of developing the Data Dictionary for GC Organics and Wet-Chemistry Parameters. This information will be provided to the laboratory when it becomes available.

When submitted, floppy diskettes shall be packaged and shipped in such a manner that the diskette(s) cannot be bent or folded, and will not be exposed to extreme heat or cold or any type of electromagnetic radiation. The diskette(s) must be included in the same shipment as the hardcopy data and shall, at a minimum, be enclosed in a diskette mailer.

G. - GC/MS Tapes

The Laboratory must store <u>all</u> raw and processed GC/MS data on magnetic tape, in appropriate instrument manufacturer's format. This tape must include data for samples, blanks, matrix spikes, matrix spike duplicates, initial calibrations, continuing calibrations, BFB and DFTPP, as well as all laboratory-generated spectral libraries and quantitation reports required to generate the data package. The Laboratory shall maintain a written

reference logbook of tape files to DEC sample number, calibration data, standards, blanks, matrix spikes, and matrix spike duplicates. The logbook should include DEC sample numbers and standard and blank ID's, identified by Case and Sample Delivery Group.

The Laboratory is required to retain the GC/MS tapes for 365 days after data submission. During that time, the Laboratory shall submit tapes and associated logbook pages within seven days after receipt of a written request from the Bureau of Watershed Assessment and Research.

See Exhibit E for specific requirements.

H. - Extracts

The Laboratory shall preserve sample extracts at 4°C (±2°C) in bottles/vials with Teflon-lined septa. Extract bottles/vials shall be labeled with NYSDEC sample number, Case number and Sample Delivery Group (SDG) number. A logbook of stored extracts shall be maintained, listing NYSDEC sample number and associated Case and SDG numbers.

The Laboratory is required to retain extracts for 90 days following data submission. During that time, the Laboratory shall submit extracts and associated logbook pages within seven days following receipt of a written request from the Bureau of Technical Services and Research or the Project Officer.

I. - Complete SDG File Purge

As specified in the Delivery Schedule, one Complete SDG File (CSF) including the original Sample Data Package shall be delivered to the BWAR concurrently with delivery of the Sample Data Package to the sample submitter or Project Director. The contents of the CSF will be numbered according to the specifications described in Section III and IV of Exhibit B. The Document Inventory Sheet, Form DC-2, is contained in Section IV. The CSF will contain all original documents where possible. No copies will be placed in the CSF unless the originals are bound in a logbook which is maintained by the Laboratory. The CSF will contain all original documents specified in Section III and IV, and Form DC-2 of Exhibit B of this Protocol.

The CSF will consist of the following original documents in addition to the documents in the Sample Data Package:

1. Original Sample Data Package

2. A completed and signed Document Inventory Sheet (Form DC-2).

3. All original shipping documents, including, but not limited to, the following documents:

    a. NYSDEC Chain of Custody Record.

    b. Airbills.

    c. NYSDEC Contract Lab Sample Information Sheets.

    d. Sample Tags (if present) sealed in plastic bags.

4. All original receiving documents, including, but not limited to, the following documents:

a. Form DC-1.

b. Other receiving forms or copies of receiving logbooks.

c. SDG Cover Sheet.

5. All original laboratory records, not already submitted in the Sample Data Package, of sample transfer, preparation and analysis, including, but not limited to, the following documents:

a. Original preparation and analysis forms or copies of preparation and analysis logbook pages.

b. Internal sample and sample extract transfer chain-of-custody records.

c. Screening records.

d. All instrument output, including strip charts from screening activities.

6. All other original SDG-specific documents in the possession of the Laboratory, including, but not limited to, the following documents:

a. Telephone contact logs.

b. Copies of personal logbook pages.

c. All hand written case-specific notes.

d. Any other case-specific documents not covered by the above.

***NOTE**: All Case-related documentation may be used or admitted as evidence in subsequent legal proceedings. Any other Case-specific documents generated after the CSF is sent to NYSDEC, as well as copies that are altered in any fashion, are also deliverables to NYSDEC.*

If the Laboratory does submit SDG-specific documents to NYSDEC after submission of the CSF, the documents should be numbered as an addendum to the CSF and a revised DC-2 form should be submitted, or the documents should be numbered as a new CSF and a new DC-2 form should be submitted to the BWAR only.

(Formerly, Document Control and Chain-of-Custody Package).

The Complete SDG File Purge includes all laboratory records received or generated for a specific SDG that have not been previously submitted to DEC as a deliverable. These items include but are not limited to: sample tags, custody records, sample tracking records, analysts logbook pages, bench sheets, chromatographic charts, computer printouts, raw data summaries, instrument logbook pages, correspondence, and the document inventory (see Exhibit F).

Shipment of the Complete SDG File Purge package by first class mail, overnight carrier, priority mail or equivalent is acceptable. Custody seals must be placed on shipping containers and a document inventory and transmittal letter included. The Laboratory is not required to maintain any documents for a sample SDG after submission of the

Complete SDG File Purge package; however, the Laboratory should maintain a copy of the document inventory and transmittal letter.

J. - Semiannual Verification of Instrument Parameters

The Laboratory shall perform and report semiannually verification of instrument detection limits and linear range by methods specified in Exhibit E for each instrument used under this Protocol. For the ICP instrumentation and methods, the Laboratory shall also report annually interelement correction factors (including method of determination), wavelengths used, and integration times. Semiannual Verification of Instrument Parameters forms for the current period shall be submitted in each Sample Delivery Group data package, using Forms X, XI and XII. Submission of Semiannual Verification of Instrument Parameters shall include the raw data used to determine those values reported.

Section III -- CLP Reporting Forms and Instruction Guide

Required Organic and Inorganic Reporting forms and instructions for completion of the forms can be found in Exhibit D, CLP.

Section IV -- NYSDEC Data Package Summary Forms

I. Sample Identification and Analytical Requirement Summary (Page 1 of 6)

A. Customer Sample Code

Sample code number (assigned by sampling crew). A number must be given to each sample to be analyzed and documented on form.

B. Laboratory Sample Code

Code number given to respective sample by the laboratory and used for identification throughout analysis. If sample receives laboratory sample numbers, please indicate on page 1.

C. Analytical Requirements

1. Check appropriate boxes for parameters to be analyzed.

2. Circle either CLP or Non-CLP and enter year of protocol. If non-CLP, circle type of analyses needed, if necessary, provide analysis as an attachment sheet.

II. Sample Preparation and Analysis Summary, B/N-A, Pesticides/PCB's and VOA

(Pages 2,3,4 of 7)

A. Sample ID

The sample code number which the laboratory will use throughout the analysis for a specific sample.

B. Matrix

Label the sample with matrix of either water, soil, oil, grease, drum solvent, etc.

C. Date Collected

Record the date that sample was collected on site.

D. Date Received at Laboratory

Record the date the Laboratory received the sample. (Verified Time of Sample Receipt - VTSR)

E. Date Extracted

Record the date the sample was extracted.

F. Date Analyzed

Record the date the sample was analyzed.

III. Sample Preparation and Analysis Summary - Organic Analysis

A. Sample ID

The sample code number which the laboratory will use throughout analysis for a specific sample.

B. Matrix

Label the sample with the specific matrix (see #B).

C. Analytical Protocol

Record year and Protocol used (i.e., 2000 NYSDEC ASP or 1989 NYSDEC ASP - Revision 10/95). If non-CLP, list number of method used.

D. Extraction Method

Write the method used for sample extraction.

E. Auxiliary Clean-Up

If cleanup was done on sample, record the method or methods used.

F. Dil/Con Factor

If sample was diluted, record the dilution factor, or if concentrated, record also.

IV. Sample Preparation and Analysis Summary - Inorganics Analysis

A. Sample ID and Matrix columns are completed following procedures for VOA, BNA, Pesticides/PCB's.

B. Metals Requested

List metals that are to be analyzed. If for NYSDEC ASP, write full TCL in column, or more individual metals required.

C. Date Received - VTSR

D. Date Digested

E. Date Analyzed

Date sample was analyzed on instrument.

To be included with all lab data and with each workplan

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

SAMPLE IDENTIFICATION AND ANALYTICAL REQUIREMENT SUMMARY

Customer Sample Code	Laboratory Sample Code	Analytical Requirements					
		*VOA GC/MS Method #	*BNA GC/MS Method #	*VOA GC Method #	*Pest PCBs Method #	*Metals	*Other

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

SAMPLE PREPARATION AND ANALYSIS SUMMARY
SEMIVOLATILE (BNA)
ANALYSES

Laboratory Sample ID	Matrix	Date Collected	Date Rec'd at Lab	Date Extracted	Date Analyzed

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

SAMPLE PREPARATION AND ANALYSIS SUMMARY
VOLATILE (VOA)
ANALYSES

Laboratory Sample ID	Matrix	Date Collected	Date Rec'd at Lab	Date Extracted	Date Analyzed

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

SAMPLE PREPARATION AND ANALYSIS SUMMARY
PESTICIDE/PCB
ANALYSES

Laboratory Sample ID	Matrix	Date Collected	Date Rec'd at Lab	Date Extracted	Date Analyzed

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

SAMPLE PREPARATION AND ANALYSIS SUMMARY
SEMIVOLATILE (BNA)
ANALYSES

Laboratory Sample ID	Matrix	Analytical Protocol	Extraction Method	Auxiliary Cleanup	Dil/Conc Factor

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

SAMPLE PREPARATION AND ANALYSIS SUMMARY
INORGANIC ANALYSES

Laboratory Sample ID	Matrix	Metals Requested	Date Rec'd at Lab	Date Analyzed

EXHIBIT C

TARGET COMPOUND LISTS (TCLs)

AND

CONTRACT REQUIRED QUANTITATION LIMITS (CRQLs)

Table of Contents

Introduction

NOTE: The values in these tables are quantitation limits, not absolute detection limits. The amount of material necessary to produce a detector response that can be identified and reliably quantified is greater than that needed to simply be detected above the background noise. The quantitation limits in these tables are set at the concentrations in the sample equivalent to the concentration of the lowest calibration standard analyzed for each analyte.

Specific quantitation limits are highly matrix dependent. The quantitation limits listed herein are provided for guidance and may not always be achievable.

CRQL values listed on the following pages are based on the analysis of samples according to the specifications given in Exhibit D. For each fraction and matrix, a brief synopsis of the sample handling and analysis steps is given, along with an example calculation for the CRQL value. All CRQL values are rounded to two significant figures. For soil samples, the moisture content of the samples is not considered in these example calculations.

Section I -- Superfund-CLP Organics

Superfund Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)

	Volatiles	CAS Number	Quantitation Limits* Water µg/L	Low Soil µg/Kg	Med Soil µg/Kg	On Column (ng)
1.	Dichlorodifluoromethane	75-71-8	10	10	1200	(50)
2.	Chloromethane	74-87-3	10	10	1200	(50)
3.	Bromomethane	74-83-9	10	10	1200	(50)
4.	Vinyl chloride	75-01-4	10	10	1200	(50)
5.	Chloroethane	75-00-3	10	10	1200	(50)
6.	Trichlorofluoromethane	75-69-4	10	10	1200	(50)
7.	1,1-Dichloroethene	75-35-4	10	10	1200	(50)
8.	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	10	10	1200	(50)
9.	Acetone	67-64-1	10	10	1200	(50)
10.	Carbon Disulfide	75-15-0	10	10	1200	(50)
11.	Methyl Acetate	79-20-9	10	10	1200	(50)
12.	Methylene chloride	75-09-2	10	10	1200	(50)
13.	trans-1,2-Dichloroethene	156-60-5	10	10	1200	(50)
14.	Methyl tert-Butyl Ether	1634-04-4	10	10	1200	(50)
15.	1,1-Dichloroethane	75-35-3	10	10	1200	(50)
16.	cis-1,2-Dichloroethene	156-59-2	10	10	1200	(50)
17.	2-Butanone	78-93-3	10	10	1200	(50)
18.	Chloroform	67-66-3	10	10	1200	(50)
19.	1,1,1-Trichloroethane	71-55-6	10	10	1200	(50)
20.	Cyclohexane	110-82-7	10	10	1200	(50)
21.	Carbon tetrachloride	56-23-5	10	10	1200	(50)
22.	Benzene	71-43-2	10	10	1200	(50)
23.	1,2-Dichloroethane	107-06-2	10	10	1200	(50)
24.	Trichloroethene	79-01-6	10	10	1200	(50)
25.	Methylcyclohexane	108-87-2	10	10	1200	(50)
26.	1,2-Dichloropropane	78-87-5	10	10	1200	(50)
27.	Bromodichloromethane	75-27-4	10	10	1200	(50)
28.	cis-1,3-Dichloropropene	10061-01-5	10	10	1200	(50)
29.	4-Methyl-2-pentanone	108-10-1	10	10	1200	(50)
30.	Toluene	108-88-3	10	10	1200	(50)
31.	trans-1,3-Dichloropropene	10061-02-6	10	10	1200	(50)
32.	1,1,2-Trichloroethane	79-00-5	10	10	1200	(50)
33.	Tetrachloroethene	127-18-4	10	10	1200	(50)
34.	2-Hexanone	591-78-6	10	10	1200	(50)
35.	Dibromochloromethane	124-48-1	10	10	1200	(50)

Superfund Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)

	Volatiles (cont.)	CAS Number	Quantitation Limits* Water µg/L	Low Soil µg/Kg	Med Soil µg/Kg	On Column (ng)
36.	1,2-Dibromoethane	106-93-4	10	10	1200	(50)
37.	Chlorobenzene	108-90-7	10	10	1200	(50)
38.	Ethyl Benzene	100-41-4	10	10	1200	(50)
39.	Total Xylenes	1330-20-7	10	10	1200	(50)
40.	Styrene	100-42-5	10	10	1200	(50)
41.	Bromoform	75-25-2	10	10	1200	(50)
42.	Isopropylbenzene	98-82-8	10	10	1200	(50)
43.	1,1,2,2-Tetrachloroethane	79-34-5	10	10	1200	(50)
44.	1,3-Dichlorobenzene	541-73-1	10	10	1200	(50)
45.	1,4-Dichlorobenzene	106-46-7	10	10	1200	(50)
46.	1,2-Dichlorobenzene	95-50-1	10	10	1200	(50)
47.	1,2-Dibromo-3-chloropropane	96-12-8	10	10	1200	(50)
48.	1,2,4-Trichlorobenzene	120-82-1	10	10	1200	(50)

* Quantitation Limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, as required by the protocol, will be higher.

Note that the CRQL values listed on the preceding page may not be those specified in previous Analytical Services Protocols. These values are set at concentrations in the sample equivalent to the concentration of the lowest calibration standard specified in Exhibit D, Part II. Lower quantitation limits may be achievable for water samples by employing the methods in Exhibit D, Part X for Low Concentration Water for Organic Analyses.

VOLATILES

Water Samples

A 5 mL volume of water is purged with an inert gas at ambient temperature. The volatiles are trapped on solid sorbents, and desorbed directly onto the GC/MS. For a sample with compound X at the CRQL of 10 µg/L:

(10 µg/L) (5 mL) (10^{-3} L/mL) = 50 x 10^{-3} ug = 50 ng on the GC column

Low Level Soil/Sediment Samples

A 5 g aliquot of the soil/sediment sample is added to a volume of water in a purge tube, heated, and purged with an inert gas. The volatiles are trapped, and later desorbed directly onto the GC/MS. For a sample with compound X at the CRQL of 10 µg/Kg:

(10 µg/Kg) (5 g) (10^{-3} Kg/g) = 50 x 10^{-3} µg = 50 ng on the GC column

Medium Level Soil/Sediment Samples

A 4 g aliquot of soil/sediment is extracted with 10 mL of methanol, and filtered through glass wool. Only 1 mL of the methanol extract is taken for screening and analysis. Based on the results of a GC/FID screen, an aliquot of the methanol extract is added to 5 mL of reagent water and purged at ambient temperature. The largest aliquot of extract considered in Exhibit D, Part III is 100 uL. For a sample with compound X at the CRQL of 1200 µg/Kg:

(1200 µg/Kg) (4 g) (10^{-3} Kg/g) = 4800 x 10^{-3} µg = 4800 ng

This material is contained in the 10 mL methanol extract:

(4800 ng) / 10 mL = 480 ng/mL

Of which, 100 µL are purged from the reagent water.

(480 ng/mL) (100 µL) (10^{-3} mL/µL) = 480 x 10^{-1} ng = 50 ng on the GC column

Note that for both low and medium soil/sediment samples, while it may affect the purging efficiency, the volume of reagent water used in the purging process does not affect the calculations.

Superfund Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)*

	Semivolatiles	CAS Number	Quantitation Limits* Water µg/L	Low Soil µg/Kg	Med Soil µg/Kg	On Column (ng)
34.	Phenol	108-95-2	10	330	10,000	(20)
35.	bis(2-Chloroethyl) ether	111-44-4	10	330	10,000	(20)
36.	2-Chlorophenol	95-57-8	10	330	10,000	(20)
37.	1,3-Dichlorobenzene	541-73-1	10	330	10,000	(20)
38.	1,4-Dichlorobenzene	106-46-7	10	330	10,000	(20)
39.	1,2-Dichlorobenzene	95-50-1	10	330	10,000	(20)
40.	2-Methylphenol	95-48-7	10	330	10,000	(20)
41.	2,2'-oxybis(1-Chloro-propane) #	108-60-1	10	330	10,000	(20)
42.	4-Methylphenol	106-44-5	10	330	10,000	(20)
43.	N-Nitroso-di-n-propylamine	621-64-7	10	330	10,000	(20)
44.	Hexachloroethane	67-72-1	10	330	10,000	(20)
45.	Nitrobenzene	98-95-3	10	330	10,000	(20)
46.	Isophorone	78-59-1	10	330	10,000	(20)
47.	2-Nitrophenol	88-75-5	10	330	10,000	(20)
48.	2,4-Dimethylphenol	105-67-9	10	330	10,000	(20)
49.	bis(2-Chloroethoxy) methane	111-91-1	10	330	10,000	(20)
50.	2,4-Dichlorophenol	120-83-2	10	330	10,000	(20)
51.	1,2,4-Trichlorobenzene	120-82-1	10	330	10,000	(20)
52.	Naphthalene	91-20-3	10	330	10,000	(20)
53.	4-Chloroaniline	106-47-8	10	330	10,000	(20)
54.	Hexachlorobutadiene	87-68-3	10	330	10,000	(20)
55.	4-Chloro-3-methylphenol	59-50-7	10	330	10,000	(20)
56.	2-Methylnaphthalene	91-57-6	10	330	10,000	(20)
57.	Hexachlorocyclopentadiene	77-47-4	10	330	10,000	(20)
58.	2,4,6-Trichlorophenol	88-06-2	10	330	10,000	(20)
59.	2,4,5-Trichlorophenol	95-95-4	25	800	25,000	(50)
60.	2-Chloronaphthalene	91-58-7	10	330	10,000	(20)
61.	2-Nitroaniline	88-74-4	25	800	25,000	(50)
62.	Dimethyl phthalate	131-11-3	10	330	10,000	(20)
63.	Acenaphthylene	208-96-8	10	330	10,000	(20)
64.	2,6-Dinitrotoluene	606-20-2	10	330	10,000	(20)
65.	3-Nitroaniline	99-09-2	25	800	25,000	(50)
66.	Acenaphthene	83-32-9	10	330	10,000	(20)

Previously known by the name bis(2-Chloroisopropyl) ether

Superfund Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)

	Semivolatiles	CAS Number	Quantitation Limits* Water µg/L	Low Soil µg/Kg	Med Soil µg/Kg	On Column (ng)
67.	2,4-Dinitrophenol	51-28-5	25	800	25,000	(50)
68.	4-Nitrophenol	100-02-7	25	800	25,000	(50)
69.	Dibenzofuran	132-64-9	10	330	10,000	(20)
70.	2,4-Dinitrotoluene	121-14-2	10	330	10,000	(20)
71.	Diethylphthalate	84-66-2	10	330	10,000	(20)
72.	4-Chlorophenyl phenyl ether	7005-72-3	10	330	10,000	(20)
73.	Fluorene	86-73-7	10	330	10,000	(20)
74.	4-Nitroaniline	100-01-6	25	800	25,000	(50)
75.	4,6-Dinitro-2-methylphenol	534-52-1	25	800	25,000	(50)
76.	N-nitrosodiphenylamine	86-30-6	10	330	10,000	(20)
77.	4-Bromophenyl phenyl ether	101-55-3	10	330	10,000	(20)
78.	Hexachlorobenzene	118-74-1	10	330	10,000	(20)
79.	Pentachlorophenol	87-86-5	25	800	25,000	(50)
80.	Phenanthrene	85-01-8	10	330	10,000	(20)
81.	Anthracene	120-12-7	10	330	10,000	(20)
82	Carbazole	86-74-8	10	330	10,000	(20)
83.	Di-n-butyl phthalate	84-74-2	10	330	10,000	(20)
84.	Fluoranthene	206-44-0	10	330	10,000	(20)
85.	Pyrene	129-00-0	10	330	10,000	(20)
86.	Butyl benzyl phthalate	85-68-7	10	330	10,000	(20)
87.	3,3'-Dichlorobenzidine	91-94-1	10	330	10,000	(20)
88.	Benz[a]anthracene	56-55-3	10	330	10,000	(20)
89.	Chrysene	218-01-9	10	330	10,000	(20)
90.	bis(2-Ethylhexyl)phthalate	117-81-7	10	330	10,000	(20)
91.	Di-n-octyl phthalate	117-84-0	10	330	10,000	(20)
92.	Benzo[b]fluoranthene	205-99-2	10	330	10,000	(20)
93.	Benzo[k]fluoranthene	207-08-9	10	330	10,000	(20)
94.	Benzo[a]pyrene	50-32-8	10	330	10,000	(20)
95.	Indeno(1,2,3-cd]pyrene	193-39-5	10	330	10,000	(20)
96.	Dibenz[a,h]anthracene	53-70-3	10	330	10,000	(20)
97.	Benzo[g,h,i]perylene	191-24-2	10	330	10,000	(20)

* Quantitation limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the Laboratory for soil/sediment, calculated on dry weight basis as required by the Protocol, will be higher.

SEMIVOLATILES

Water Samples

A 1 L volume of water is extracted in a continuous liquid-liquid extractor with methylene chloride at a pH of approximately 2. This extract is reduced in volume to 1.0 mL, and a 2 µL volume is injected onto the GC/MS for analysis. For a sample with compound X at the CRQL of 10 µg/L:

(10 µg/L) (1 L) = 10 µg in the original extract

When the extract is concentrated, this .material is contained in the 1 mL concentrated extract, of which 2 µL are injected into the instrument:

(10 µg/mL) (2 µL) (10^{-3} mL/µL) = 20 x 10^{-3} µg = 20 ng on the GC column

Low Soil Samples

A 30 g soil sample is extracted three times with methylene chloride/acetone at ambient pH, by sonication or Soxhlet. The extract is reduced in volume to 1.0 mL, and a 2 µL volume is injected onto the GC/MS for analysis. For a sample with compound X at the CRQL of 330 µg/Kg:

(330 µg/Kg) (30 g) (10^{-3} Kg/g) = 9900 x 10^{-3} µg = 9.9 µg

When the sample extract is to be subjected to Gel Permeation Chromatography (required) to remove high molecular weight interferences, the volume of the extract is initially reduced to 10 mL. This 10 mL is put through the GPC column, and only 5 mL are collected off the GPC. That 5 mL volume is reduced to 0.5 mL prior to analysis. Therefore:

(9.9 µg/10 mL) (5 mL) = 4.95 µg

This material is contained in the 0.5 mL extract, of which 2 µL are injected lnto the instrument:

(4.95 µg/0.5 mL) (2 µL) (10^{-3} mL/µL) = (1.98 x 10^{-2} µg) 20 ng on the GC column

Medium Soil Samples

A 1 g soil sample is extracted once with 10 mL of methylene chloride/acetone, which is filtered through glass wool to remove particles of soil. The filtered extract is then subjected to GPC clean up, and only 5 mL of extract are collected after GPC. This extract is reduced in volume to 0.5 mL, of which 2 µL are injected onto the GC/MS. For a sample with compound X at the CRQL of 10,000 µg/Kg:

(10,000 µg/Kg) (1 g) (10^{-3} Kg/g) = 10 µg

(continued)

Semivolatiles, Medium Soil, continued -

This material is contained in the 10 mL extract, of which only 5 mL are collected after GPC:

(10 µg) (5 mL/10 mL) = 5 ug

The volume of this extract is reduced to 0.5 mL, of which 2 µL are injected into the instrument:

(5 µg/0.5 mL) (2 µL) (10^{-3} mL/µL) = 20 x 10^{-3} ug = 20 ng on the GC column

Eight semivolatile compounds are calibrated using only a four point initial calibration, with the lowest standard at 50 ng. Therefore, the CRQL values for these eight compounds are 2.5 times higher for all matrices and levels.

Superfund Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)*

	Pesticides/Aroclors	CAS Number	Quantitation Limits* Water µg/L	Soil µg/Kg	On Column (pg)
98.	alpha-BHC	319-84-6	0.05	1.7	5
99.	beta-BHC	319-85-7	0.05	1.7	5
100.	delta-BHC	319-86-8	0.05	1.7	5
101.	gamma-BHC (Lindane)	58-89-9	0.05	1.7	5
102.	Heptachlor	76-44-8	0.05	1.7	5
103.	Aldrin	309-00-2	0.05	1.7	5
104.	Heptachlor epoxide	1024-57-3	0.05	1.7	5
105.	Endosulfan I	959-98-8	0.05	1.7	5
106.	Dieldrin	60-57-1	0.10	3.3	10
107.	4,4'-DDE	72-55-9	0.10	3.3	10
108.	Endrin	72-20-8	0.10	3.3	10
109.	Endosulfan II	33213-65-9	0.10	3.3	10
110.	4,4'-DDD	72-54-8	0.10	3.3	10
111.	Endosulfan sulfate	1031-07-8	0.10	3.3	10
112.	4,4'-DDT	50-29-3	0.10	3.3	10
113.	Methoxychlor	72-43-5	0.50	17.0	50
114.	Endrin ketone	53494-70-5	0.10	3.3	10
115.	Endrin aldehyde	7421-36-3	0.10	3.3	10
116.	alpha-Chlordane	5103-71-9	0.05	1.7	5
117.	gamma-Chlordane	5103-74-2	0.05	1.7	5
118.	Toxaphene	8001-35-2	5.0	170.0	500
119.	AROCLOR-1016	12674-11-2	1.0	33.0	100
120.	AROCLOR-1221	11104-28-2	2.0	67.0	200
121.	AROCLOR-1232	11141-16-5	1.0	33.0	100
122.	AROCLOR-1242	53469-21-9	1.0	33.0	100
123.	AROCLOR-1248	12672-29-6	1.0	33.0	100
124.	AROCLOR-1254	11097-69-1	1.0	33.0	100
125.	AROCLOR-1260	11096-82-5	1.0	33.0	100

* Quantitation Limits listed for soil/sediment are based on wet weight. The quantitation limits calculated by the Laboratory for soil/sediment, calculate on dry weight basis, as required by the Protocol, will be higher.

PESTICIDES/AROCLORS

Water Samples

A 1 L volume of water is extracted three times with methylene chloride or by a continuous liquid-liquid extractor. This extract is reduced in volume to approximately 3 - 5 mL, and diluted up to 10.0 mL with clean solvent. When Gel Permeation Chromatography is performed, only 5 of the 10 mL of extract are collected after GPC.

Regardless of whether GPC is performed, either 1.0 or 2.0 mL of the 10.0 mL of the original extracts are taken through the remaining clean up steps (Florisil and sulfur removal). The volume taken through Florisil cleanup and the final volume of the extract after the clean up steps depends on the requirements of the autosampler. If the autosampler can handle 1.0 mL final extract volumes, this is the volume taken through Florisil and the final volume. If the autosampler cannot reliably handle 1.0 mL volumes, the volume is 2.0 mL. When using an autosampler, the injection volume may be 1.0 or 2.0 µL. Manual injections must use a 2.0 µL injection volume.

For a sample with compound X at the CRQL of 0.05 µg/L and an autosampler requiring a 1.0 mL volume:

(0.05 µg/L) (1 L) = 0.05 µg in the original extract

This material is contained in the 10.0 mL of extract:

(0.05 µg)/ (10.0 mL) = 0.005 µg/mL

Of which, only 1.0 mL is carried through the remaining clean up steps. For a final extract volume of 1.0 mL and a 1 µL injection volume:

(0.005 µg/L) (1 µL) (10^{-3} mL/µL) = 5 x 10^{-6} µg = 5 pg on the GC column

Soil Samples

There is no differentiation between the preparation of low and medium soil samples in this method for the analysis of pesticides/Aroclors. A 30 g soil sample is extracted three times with methylene chloride/acetone by sonication or Soxhlet extraction. The extract is reduced in volume to 10.0 mL and subjected to Gel Permeation Chromatography. After GPC, only 5.0 mL of extract are collected. However, as with the water sample described above, either 1.0 or 2.0 mL of that extract are subjected to the other clean up steps, so no loss of sensitivity results from the use of GPC. From this point on, the soil sample extract is handled in the same fashion as the extract of a water sample. For a sample with compound X at the CRQL of 1.7 µg/Kg:

(1.7 µg/Kg) (30 g) (10^{-3} Kg/g) = 51 x 10^{-3} µg = 51 ng in the original extract

This material is contained in the 10.0 mL of extract:

(51 ng)/10 mL = 5.1 ng/mL
(continued)

of which, only 1.0 or 2.0 mL are carried through the remaining cleanup steps For a final extract volume of 1.0 mL and a 1 µL injection volume:

$(5.1\ ng/mL)(1\ \mu L)(10^{-3}\ mL/\mu L) = 5.1 \times 10^{-3}\ ng = 5\ pg$ on the GC column.

For either water or soil samples, if the autosampler used requires a 2.0 mL final volume, the concentration in the 10.0 mL of extract above remains the same.

Using a 2 µL injection volume, twice the total number of picograms are injected onto the GC column. However, because the injection volume must be the same for samples and standards, twice as much material is injected onto the column during calibration, and thus the amount of compound X injected from the sample extract is equivalent to the amount of compound X injected from the calibration standard, regardless of injection volume.

If a single injection is used for two GC columns attached to a single injection part, it may be necessary to use an injection volume greater than 2 µL.

Section II -- Superfund-CLP Inorganics

Superfund Target Compound List (TCL) and
Contract Required Quantitation Limit

	Parameter	Contract Required Quantitation Level (µg/L)
1.	Aluminum	200
2.	Antimony	60
3.	Arsenic	10
4.	Barium	200
5.	Beryllium	5
6.	Cadmium	5
7.	Calcium	5000
8.	Chromium	10
9.	Cobalt	50
10.	Copper	25
11.	Iron	100
12.	Lead	3
13.	Magnesium	5000
14.	Manganese	15
15.	Mercury	0.2
16.	Nickel	40
17.	Potassium	5000
18.	Selenium	5
19.	Silver	10
20.	Sodium	5000
21.	Thallium	10
22.	Vanadium	50
23.	Zinc	20
24.	Cyanide	10

1: Any analytical method specified in Exhibit D, CLP-Inorganics may be utilized as long as the documented instrument or method detection limits meet the Contract Required Quantitation Level (CRQL) requirements. Higher quantitation levels may only be used in the following circumstance:

If the sample concentration exceeds five times the quantitation limit of the instrument or method in use, the value may be reported even though the instrument or method detection limit may not equal the Contract Required Quantitation Limit. This is illustrated in the example below:

For lead:
Method in use = ICP
Instrument Detection Limit (IDL) = 40
Sample concentration = 220
Contract Required Quantitation Level (CRQL) = 3

The value of 220 may be reported even though instrument detection limit is greater than Contract Required Quantitation Limit. The instrument or method detection limit must be documented as described in Exhibit E.

2: These CRQLs are the instrument detection limits obtained in pure water that must be met using the procedure in Exhibit E. The quantitation limits for samples may be considerably higher depending on the sample matrix.

Section III -- Regulatory Promulgated Parameters

In addition to the preceding lists, the Laboratory may be asked to analyze for any or all of the conventional water quality parameters as listed in 40CFR Part 136 or for the hazardous waste parameters listed in 40CFR Part 260 through 270.

Quantitation limits to be achieved for these analyses are specified.

A. -- 40CFR Part 136 Parameters

Target Compound List (TCL) and
Contract Required Quantitation Limit

Parameter		Contract Required Quantitation Level (µg/L)
Conventionals		
1.	Biochemical Oxygen Demand (BOD5)	2,000
2.	Chemical Oxygen Demand (COD)	1,000
3.	Total Dissolved Solids (TDS)	10,000
4.	Total Suspended Solids (TSS)	10,000
5.	Ammonia, as N	50
6.	Total Kjeldahl Nitrogen, as N	100
7.	Nitrate-Nitrite	100
8.	Total Phosphorus	50
9.	Reactive Phosphorus	10
10.	Sulfate	5,000
11.	Oil and Grease	5,000
12.	Total Organic Carbon	2,000
13.	Total Phenols	10
14.	Chloride	5,000
15.	Fluoride	500
16.	Cyanide	10
Metals		
17.	Aluminum	200
18.	Antimony	60
19.	Arsenic	10
20.	Barium	200
21.	Beryllium	5
22.	Cadmium	5
23.	Calcium	5,000
24.	Chromium	10
25.	Cobalt	50
26.	Copper	25
27.	Gold	10
28.	Iridium	200
29.	Iron	100
30.	Lead	5
31.	Magnesium	5,000
32.	Manganese	15

40CFR Part 136 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Level (µg/L)
Metals (cont.)			
33.	Mercury		0.2
34.	Molybdenum		10
35.	Nickel		40
36.	Osmium		100
37.	Palladium		100
38.	Platinum		200
39.	Potassium		5,000
40.	Rhenium		5,000
41.	Rhodium		100
42.	Ruthenium		500
43.	Selenium		5
44.	Silver		10
45.	Sodium		5,000
46.	Thallium		10
47.	Tin		40
48.	Titanium		100
49.	Vanadium		50
50.	Zinc		20
Volatile Organics (Method 624)			
1.	Chloromethane	74-87-3	10
2.	Bromomethane	74-83-9	10
3.	Vinyl chloride	75-01-4	10
4.	Chloroethane	75-00-3	10
5.	Methylene chloride	75-09-2	5
6.	1,1-Dichloroethene	75-35-4	5
7.	1,1-Dichloroethane	75-35-3	5
8.	trans-1,2-Dichloroethene	156-60-5	5
9.	Chloroform	67-66-3	5
10.	1,2-Dichloroethane	107-06-2	5
11.	1,1,1-Trichloroethane	71-55-6	5
12.	Carbon tetrachloride	56-23-5	5
13.	Bromodichloromethane	75-27-4	5

40CFR Part 136 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Level (µg/L)
Volatile Organics (Method 624 cont.)			
14.	1,1,2,2-Tetrachloroethane	79-34-5	5
15.	1,2-Dichloropropane	78-87-5	5
16.	trans-1,3-Dichloropropene	10061-02-6	5
17.	Trichloroethene	79-01-6	5
18.	Dibromochloromethane	124-48-1	5
19.	1,1,2-Trichloroethane	79-00-5	5
20.	Benzene	71-43-2	5
21.	cis-1,3-Dichloropropene	10061-01-5	5
22.	2-Chloroethyl vinyl ether	110-75-8	10
23.	Bromoform	75-25-2	5
24.	Tetrachloroethene	127-18-4	5
25.	Toluene	108-88-3	5
26.	Chlorobenzene	108-90-7	5
27.	Ethyl Benzene	100-41-4	5
28.	1,3-Dichlorobenzene	541-73-1	10
29.	1,4-Dichlorobenzene	106-46-7	10
30.	1,2-Dichlorobenzene	95-50-1	10
31.	Trichlorofluoromethane	75-69-4	10
Volatile Organics (Method 601)			
1.	Chloromethane	74-87-3	0.5
2.	Bromomethane	74-83-9	5
3.	Vinyl chloride	75-01-4	1.0
4.	Chloroethane	75-00-3	5
5.	Methylene chloride	75-09-2	1.0
6.	1,1-Dichloroethene	75-35-4	0.1
7.	1,1-Dichloroethane	75-35-3	0.5
8.	trans-1,2-Dichloroethene	156-60-5	0.5
9.	Chloroform	67-66-3	0.5
10.	1,2-Dichloroethane	107-06-2	0.1
11.	1,1,1-Trichloroethane	71-55-6	0.1
12.	Carbon tetrachloride	56-23-5	0.5
13.	Bromodichloromethane	75-27-4	0.5

40CFR Part 136 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Level (µg/L)
Volatile Organics (Method 601 cont.)			
14.	1,1,2,2-Tetrachloroethane	79-34-5	0.1
15.	1,2-Dichloropropane	78-87-5	0.5
16.	trans-1,3-Dichloropropene	10061-02-6	1.0
17.	Trichloroethene	79-01-6	0.5
18.	Dibromochloromethane	124-48-1	0.5
19.	1,1,2-Trichloroethane	79-00-5	0.1
21.	cis-1,3-Dichloropropene	10061-01-5	0.5
22.	2-Chloroethyl vinyl ether	110-75-8	0.5
23.	Bromoform	75-25-2	1.0
24.	Tetrachloroethene	127-18-4	0.1
25.	Chlorobenzene	108-90-7	1.0
26.	1,2-Dichlorobenzene	95-50-1	1.0
27.	1,3-Dichlorobenzene	541-73-1	1.0
28.	1,4-Dichlorobenzene	106-46-7	1.0
29.	Trichlorofluoromethane	106-46-7	2.0
Volatile Organics (Method 602)			
1.	Benzene	71-43-2	1.0
2.	Toluene	108-88-3	1.0
3.	Chlorobenzene	108-90-7	1.0
4.	Ethyl Benzene	100-41-4	1.0
5.	1,3-Dichlorobenzene	541-73-1	1.0
6.	1,4-Dichlorobenzene	106-46-7	1.0
7.	1,2-Dichlorobenzene	95-50-1	1.0
Semivolatile Organics (Method 625)			
1.	N-Nitrosodimethylamine	62-75-9	10
2.	Phenol	108-95-2	10
3.	bis(2-Chloroethyl) ether	111-44-4	10
4.	2-Chlorophenol	95-57-8	10
5.	1,3-Dichlorobenzene	541-73-1	10

40CFR Part 136 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

	Parameter	CAS Number	Contract Required Quantitation Level (µg/L)
Semivolatile Organics (Method 625 cont.)			
6.	1,4-Dichlorobenzene	106-46-7	10
7.	1,2-Dichlorobenzene	95-50-1	10
8.	2,2'-oxybis(1-Chloropropane)	108-60-1	10
9.	N-Nitrosodi-n-propylamine	621-64-7	10
10.	Hexachloroethane	67-72-1	10
11.	Nitrobenzene	98-95-3	10
12.	Isophorone	78-59-1	10
13.	2-Nitrophenol	88-75-5	10
14.	2,4-Dimethylphenol	105-67-9	10
15.	bis(2-Chloroethoxy) methane	111-91-1	10
16.	2,4-Dichlorophenol	120-83-2	10
17.	1,2,4-Trichlorobenzene	120-82-1	10
18.	Naphthalene	91-20-3	10
19.	Hexachlorobutadiene	87-68-3	10
20.	4-Chloro-3-methylphenol (p-chloro-m-cresol)	59-50-7	10
21.	Hexachlorocyclopentadiene	77-47-4	10
22.	2,4,6-Trichlorophenol	88-06-2	10
23.	2-Chloronaphthalene	91-58-7	10
24.	Dimethyl phthalate	131-11-3	10
25.	Acenaphthylene	208-96-8	10
26.	Acenaphthene	83-32-9	10
27.	2,4-Dinitrophenol	51-28-5	50
28.	4-Nitrophenol	100-02-7	50
29.	2,4-Dinitrotoluene	121-14-2	10
30.	2,6-Dinitrotoluene	606-20-2	10
31.	Diethylphthalate	84-66-2	10
32.	4-Chlorophenyl phenyl ether	7005-72-3	10
33.	Fluorene	86-73-7	10
34.	4,6-Dinitro-2-methylphenol	534-52-1	50
35.	N-nitroso diphenylamine	86-30-6	10
36.	4-Bromophenyl phenyl ether	101-55-3	10
37.	Hexachlorobenzene	118-74-1	10
38.	Pentachlorophenol	87-86-5	50

40CFR Part 136 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

	Parameter	CAS Number	Contract Required Quantitation Level (µg/L)
Semivolatile Organics (Method 625 cont.)			
39.	Phenanthrene	85-01-8	10
40.	Anthracene	120-12-7	10
41.	Di-n-butyl phthalate	84-74-2	10
42.	Fluoranthene	206-44-0	10
43.	Benzidine	92-87-5	80
44.	Pyrene	129-00-0	10
45.	Butyl benzyl phthalate	85-68-7	10
46.	3,3'-Dichlorobenzidine	91-94-1	20
47.	Benz[a]anthracene	56-55-3	10
48.	bis(2-ethylhexyl)phthalate	117-81-7	10
49.	Chrysene	218-01-9	10
50.	Di-n-octyl phthalate	117-84-0	10
51.	Benzo[b]fluoranthene	205-99-2	10
52.	Benzo[k]fluoranthene	207-08-9	10
53.	Benzo[a]pyrene	50-32-8	10
54.	Indeno[1,2,3-cd]pyrene	193-39-5	10
55.	Dibenz[a,h]anthracene	53-70-3	10
56.	Benzo[g,h,i]perylene	191-24-2	10
Pesticides/PCBs (Method 608)			
1.	alpha-BHC	319-84-6	0.05
2.	beta-BHC	319-85-7	0.05
3.	delta-BHC	319-86-8	0.05
4.	gamma-BHC (Lindane)	58-89-9	0.05
5.	Heptachlor	76-44-8	0.05
6.	Aldrin	309-00-2	0.05
7.	Heptachlor epoxide	1024-57-3	0.05
8.	Endosulfan I	959-98-8	0.05
9.	Dieldrin	60-57-1	0.10
10.	4,4'-DDE	72-55-9	0.10
11.	Endrin	72-20-8	0.10
12.	Endosulfan II	33213-65-9	0.10
13.	4,4'-DDD	72-54-8	0.10

40CFR Part 136 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Level (µg/L)
Pesticides/PCBs (Method 608 cont.)			
14.	Endrin aldehyde	7421-93-4	0.10
15.	Endosulfan sulfate	1031-07-8	0.10
16.	4,4'-DDT	50-29-3	0.10
17.	Chlordane	57-74-9	0.5
18.	Toxaphene	8001-35-2	1.0
19.	AROCLOR-1016	12674-11-2	0.5
20.	AROCLOR-1221	11104-28-2	0.5
21.	AROCLOR-1232	11141-16-5	0.5
22.	AROCLOR-1242	53469-21-9	0.5
23.	AROCLOR-1248	12672-29-6	0.5
24.	AROCLOR-1254	11097-69-1	1.0
25.	AROCLOR-1260	11096-82-5	1.0
Other Pesticides/Herbicides			
1.	Ametryn	834-12-8	2.0
2.	Aminocarb	2032-59-9	1.0
3.	Atraton	1610-17-9	2.0
4.	Atrazine	1912-24-9	2.0
5.	Azinphos methyl	86-50-0	1.0
6.	Barban	101-27-9	0.5
7.	Captan	133-06-2	1.0
8.	Carbaryl	63-25-2	1.0
9.	Chlorpropham	101-21-3	1.0
10.	2,4-Dichlorophenoxy acetic acid; (2,4-D)	94-75-2	2.0
11.	Demeton-O	298-03-3	1.0
12.	Demeton-S	126-75-0	1.0
13.	Diazinon	333-41-5	1.0
14.	Dicamba	1918-00-9	2.0
15.	Dichloran	-	1.0
16.	Disulfoton	298-04-4	2.0
17.	Diuron	330-54-1	1.0
18.	Fenuron	101-42-8	0.5

40CFR Part 136 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Level (µg/L)
Other Pesticides and Herbicides (Continued)			
19.	Fenuron-TCA	4482-55-7	1.0
20.	Linuron	330-55-2	1.0
21.	Malathion	121-75-5	1.0
22.	Methiocarb	2032-65-7	2.0
23.	Methoxychlor	72-43-5	0.5
24.	Mexacarbate	315-18-4	1.0
25.	Mirex	2385-85-5	1.0
26.	Monuron	150-68-5	0.5
27.	Monuron-TCA	140-41-0	1.0
28.	Neburon	555-37-3	1.0
29.	Parathion ethyl	56-38-2	1.0
30.	Parathion methyl	298-00-0	1.0
31.	Pentachloronitrobenzene; (PCNB)	82-68-8	1.0
32.	Prometon	1610-18-0	2.0
33.	Prometryn	7287-19-6	2.0
34.	Propazine	139-40-2	2.0
35.	Propham	-	2.0
36.	Propoxur	114-26-1	1.0
37.	Secbumeton	26259-45-0	2.0
38.	Siduron	1982-49-6	0.5
39.	Simazine	122-34-9	2.0
40.	Strobane	-	1.0
41.	Swep	1918-18-9	2.0
42.	2,4,5-Trichlorophenoxyacetic acid; (2,4,5-T)	93-76-5	2.0
43.	(2,4,5-Trichlorophenoxy)-propionic acid; (2,4,5-TP; Silvex)	93-72-1	2.0
44.	Terbuthylazine	5915-41-3	2.0
45.	Trifluraline	1582-09-8	1.0
Dioxin			
1.	2,3,7,8-Tetrachlorodibenzo-p-dioxin; (2,3,7,8-TCDD)	1746-01-6	0.005

B -- Resource Conservation and Recovery Act (RCRA) Parameters

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit

Parameter		CAS Number	Contract Required Quantitation Level (µg/L)
A.	Ignitability (°C or °F)	NA	NA
B.	Corrosivity (pH units)	NA	NA
C.	Reactivity		
1.	Total Releasable Cyanide as HCN		100,000
2.	Total Releasable Sufide as H_2S		100,000
D.	Extraction Procedure Toxicity; (EP Tox) (concentrations in extract)		
1.	Arsenic		1,000
2.	Barium		10,000
3.	Cadmium		100
4.	Total Chromium		1,000
5.	Lead		1,000
6.	Mercury		50
7.	Selenium		100
8.	Silver		1,000
9.	gamma-BHC (Lindane)	58-89-9	100
10.	2,4-Dichlorophenoxyacetic acid; (2,4-D)	94-75-2	1,000
11.	Endrin	72-20-8	5
12.	Methoxychlor	72-43-5	1,000
13.	2,4,5-Trichlorophenoxy-propionic acid; (2,4,5-TP; Silvex)	93-72-1	100
14.	Toxaphene	8001-35-2	100

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Level (µg/L)
E.	Toxcity Charactaristic Leaching Procedure (TCLP) (concentrations in extract)		
	Metals		
1.	Arsenic		1,000
2.	Barium		10,000
3.	Cadmium		100
4.	Total Chromium		1,000
5.	Lead		1,000
6.	Mercury		50
7.	Selenium		100
8.	Silver		1,000
Volatiles			
1.	Benzene	71-43-2	10
2.	2-Butanone (Methylethylketone)	78-93-3	10
3.	Carbon tetrachloride	56-23-5	10
4.	Chlorobenzene	108-90-7	10
5.	Chloroform	67-66-3	10
6.	1,2-Dichloroethane	107-06-2	10
7.	1,1-Dichloroethylene	75-35-4	10
8.	Tetrachloroethylene	127-18-4	10
9.	Trichloroethylene	79-01-6	10
10.	Vinyl chloride	75-01-4	10
Semivolatiles			
1.	1,4-Dichlorobenzene	106-46-7	10
2.	2,4-Dinitrotoluene	121-14-2	10
3.	Hexachlorobenzene	118-74-1	10
4.	Hexachlorobutadiene	87-68-3	10
5.	Hexachloroethane	67-72-1	100
6.	2-Methylphenol (o-Cresol)	95-48-7	10
7.	3-Methylphenol (m-Cresol)	108-39-4	10
8.	4-Methylphenol (p-Cresol)	106-44-5	10
9.	Nitrobenzene	98-95-3	10

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
E.	TCLP (cont.)			
	Semivolatiles (cont.)			
10.	Pentachlorophenol	87-86-5	5	
11.	Pyridine	110-86-1	100	
12.	2,4,5-Trichlorophenol	95-95-4	10	
13.	2,4,6-Trichlorophenol	88-06-2	10	
	Pesticides			
1.	gamma-BHC (Lindane)	58-89-9	10	
2.	Chlordane	57-74-9	10	
3.	2,4-Dichlorophenoxyacetic acid; (2,4-D)	94-75-7	100	
4.	Endrin	72-20-8	0.5	
5.	Heptachlor	76-44-8	0.5	
6.	Heptachlor epoxide	1024-57-3	0.5	
7.	Methoxychlor	72-43-5	100	
8.	2,4,5-Trichlorophenoxy-propionic acid; (2,4,5-TP; Silvex)	93-76-5	10	
9.	Toxaphene	8001-35-2	10	
F.	Appendix IX Substances			
	Volatiles			
1.	Acetone	67-64-1	10	10
2.	Acetonitrile	75-05-8	100	100
3.	Acrolein	107-02-8	5	5
4.	Acrylonitrile	107-13-1	5	5
5.	Benzene	71-43-2	5	5
6.	Bromodichloromethane	75-27-4	5	5
7.	Bromoform	75-25-2	5	5
8.	Bromomethane	74-83-9	10	10
9.	2-Butanone (Methyl ethyl ketone)	78-93-3	10	10
10.	Carbon disulfide	75-15-0	5	5
11.	Carbon tetrachloride	56-23-5	5	5
12.	Chlorobenzene	108-90-7	5	5
13.	2-Chloro-1,3-butadiene	126-99-8	5	5

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
F.	Appendix IX Substances (cont.)			
	Volatiles (cont.)			
14.	Chloroethane	75-00-3	10	10
15.	Chloroform	67-66-3	5	5
16.	Chloromethane	74-87-3	10	10
17.	3-Chloropropene	107-05-1	100	100
18.	Dibromochloromethane	124-48-1	5	5
19.	1,2-Dibromo-3-chloro-propane	96-12-8	5	5
20.	1,2-Dibromoethane	106-93-4	5	5
21.	Dibromomethane	74-95-3	5	5
22.	trans-1,4-Dichloro-2-butene	110-57-6	5	5
23.	Dichlorodifluoromethane	75-71-8	5	5
24.	1,1-Dichloroethane	75-34-3	5	5
25.	1,2-Dichloroethane	107-06-2	5	5
26.	1,1-Dichloroethylene	75-35-4	5	5
27.	trans-1,2-Dichloro-ethylene	156-60-5	5	5
28.	Dichloromethane	75-09-2	5	5
29.	1,2-Dichloropropane	78-87-5	5	5
30.	cis-1,3-Dichloro-propane	10061-01-5	5	5
31.	trans-1,3-Dichloro-propane	10061-02-6	5	5
32.	1,4-Dioxane	123-91-1	150	150
33.	Ethylbenzene	100-41-4	5	5
34.	Ethylmethacrylate	97-63-2	5	5
35.	2-Hexanone	591-78-6	10	10
36.	Iodomethane	74-88-4	5	5
37.	Methacrylonitrile	126-98-7	5	5
38.	Methylmethacrylate	80-62-6	5	5
39.	4-Methyl-2-pentanone (Methyl iso-butyl ketone)	108-10-1	10	10
40.	2-Methyl-1-propanol (iso-Butyl alcohol)	78-83-1	50	50
41.	Pentachloroethane	76-01-7	5	5
42.	2-Picoline	109-06-8	5	5
43.	Propionitrile	107-12-0	5	5

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
F.	Appendix IX Substances (cont.)			
	Volatiles (cont.)			
44.	Pyridine	110-86-1	5	5
45.	Styrene	100-42-5	5	5
46.	1,1,1,2-Tetrachloro-ethane	630-20-6	5	5
47.	1,1,2,2-Tetrachloro-ethane	79-34-5	5	5
48.	Tetrachloroethylene	127-18-4	5	5
49.	Toluene	108-88-3	5	5
50.	1,1,1-Trichloroethane	71-55-6	5	5
51.	1,1,2-Trichloroethane	79-00-5	5	5
52.	Trichloroethylene	79-01-6	5	5
53.	Trichlorofluoromethane	75-69-4	5	5
54.	1,2,3-Trichloropropane	96-18-4	5	5
55.	Vinyl acetate	108-05-4	5	5
56.	Vinyl chloride	75-01-4	10	10
57.	Xylene (Total)	1330-20-7	5	5
	Semivolatiles			
58.	Acenaphthene	83-32-9	10	330
59.	Acenaphthylene	208-96-8	10	330
60.	Acetophenone	98-86-2	10	330
61.	2-Acetylaminofluorene	53-96-3	10	330
62.	4-Aminobiphenyl	92-67-1	10	330
63.	Aniline	62-53-3	10	330
64.	Anthracene	120-12-7	10	330
65.	Aramite	140-57-8	10	330
66.	Benz[a]anthracene	56-55-3	10	330
67.	Benzo[b]fluoranthene	205-99-2	10	330
68.	Benzo[k]fluoranthene	207-08-9	10	330
69.	Benzo[g.h,i]perylene	191-24-2	10	330
70.	Benzo[a]pyrene	50-32-8	10	330
71.	Benzyl alcohol	100-51-6	10	330
72.	Bis(2-chloroethoxy)-methane	111-91-1	10	330
73.	Bis(2-chloroethyl)ether	111-44-4	10	330
74.	2,2'-oxybis(1-Chloro-propane	108-60-1	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
F.	Appendix IX Substances (cont.)			
	Semivolatiles (cont.)			
75.	Bis(2-ethylhexyl)-phthalate	117-81-7	10	330
76.	4-Bromophenyl phenyl ether	101-55-3	10	330
77.	Butyl benzyl phthalate	85-68-7	10	330
78.	p-Chloroaniline	106-47-8	10	330
79.	Chlorobenzilate	510-15-6	10	330
80.	4-chloro-3-methylphenol (p-chloro-m-cresol)	59-50-7	10	330
81.	2-Chloronaphthalene	91-58-7	10	330
82.	2-Chlorophenol	95-57-8	10	330
83.	4-Chlorophenyl phenyl ether	7005-72-3	10	330
84.	Chrysene	218-01-9	10	330
85.	Diallate	2303-16-4	10	330
86.	Dibenz[a,h]anthracene	53-70-3	10	330
87.	Dibenzofuran	132-64-9	10	330
88.	Di-n-butylphthalate	84-74-2	10	330
89.	1,2-Dichlorobenzene	95-50-1	10	330
90.	1,3-Dichlorobenzene	541-73-1	10	330
91.	1,4-Dichlorobenzene	106-46-7	10	330
92.	3,3'-Dichlorobenzidine	91-94-1	20	660
93.	2,4-Dichlorophenol	120-83-2	10	330
94.	2,6-Dichlorophenol	87-65-0	10	330
95.	Diethylphthlate	84-66-2	10	330
96.	O,O-Diethyl-0-2-pyrazinyl-phosphoro-thioate	297-97-2	10	330
97.	Dimethoate	60-51-5	10	330
98.	p-(Dimethylamino)azo-benzene	60-11-7	10	330
99.	7,12-Dimethylbenz[a]-anthracene	57-97-6	10	330
100.	3,3'-Dimethylbenzidine	119-93-7	10	330
101.	a,a-Dimethylphen-ethylamine	122-09-8	10	330
102.	2,4-Dimethylphenol	105-67-9	10	330
103.	Dimethylphthlate	131-11-3	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
F.	Appendix IX Substances (cont.)			
	Semivolatiles (cont.)			
104.	1,3-Dinitrobenzene	99-65-0	10	330
105.	4,6-Dinitro-2-methyl-phenol	534-52-1	50	1,700
106.	2,4-Dinitrophenol	51-28-5	50	1,700
107.	2,4-Dinitrotoluene	121-14-2	10	330
108.	2,6-Dinitrotoluene	606-20-2	10	330
109.	Di-n-octylphthalate	117-84-0	10	330
110.	Diphenylamine	122-39-4	10	330
111.	Ethyl methanesulfonate	62-50-0	10	330
112.	Famphur	52-85-7	10	330
113	Fluoranthene	206-44-0	10	330
114.	Fluorene	86-73-7	10	330
115.	Hexachlorobenzene	118-74-1	10	330
116.	Hexachlorobutadiene	87-68-3	10	330
117.	Hexachlorocyclo-pentadiene	77-47-4	10	330
118.	Hexachlorodibenzo-p-dioxins (all isomers)		0.01	1.0
119.	Hexachlorodibenzofurans (all isomers)		0.01	1.0
120.	Hexachloroethane	67-72-1	10	330
121.	Hexachlorophene	70-30-4	10	330
122.	Hexachloropropene	1888-71-7	10	330
123.	Indeno[1,2,3-c,d]-pyrene	193-39-5	10	330
124.	Isodrin	465-73-6	10	330
125.	Isophorone	78-59-1	10	330
126.	Isosafrole	120-58-1	10	330
127.	Kepone	143-50-0	10	330
128.	Methapyrilene	91-80-5	10	330
129.	3-Methylcholanthrene	56-49-5	10	330
130.	Methyl methane sulfonate	66-27-3	10	330
131.	2-Methylnaphthalene	91-57-6	10	330
132.	2-Methylphenol (o-Cresol)	95-48-7	10	330
133.	3-Methylphenol (m-Cresol)	108-39-4	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
F.	Appendix IX Substances (cont.)			
	Semivolatiles (cont.)			
134.	4-Methylphenol (p-Cresol)	106-44-5	10	330
135.	Naphthalene	91-20-3	10	330
136.	1,4-Naphthoquinone	130-15-4	10	330
137.	1-Naphthylamine	134-32-7	10	330
138.	2-Naphthylamine	91-59-8	10	330
139.	2-Nitroaniline	88-74-4	50	1,700
140.	3-Nitroaniline	99-09-2	50	1,700
141.	4-Nitroaniline	100-01-6	50	1,700
142.	Nitrobenzene	98-95-3	10	330
143.	2-Nitrophenol	88-75-5	10	330
144.	4-Nitrophenol	100-02-7	50	1,700
145.	4-Nitroquinoline-1-oxide	56-57-5	10	330
146.	N-Nitrosodi-n-butyl-amine	924-16-3	10	330
147.	N-Nitrosodiethylamine	55-18-5	10	330
148.	N-Nitrosodimethylamine	62-75-9	10	330
149.	N-Nitrosodiphenylamine	86-30-6	10	330
150.	N-Nitrosodi-n-propyl-amine	621-24-7	10	330
151.	N-Nitrosomethylethyl-amine	10595-95-6	10	330
152.	N-Nitrosomorpholine	59-89-2	10	330
153.	N-Nitrosopiperidine	100-75-4	10	330
154.	N-Nitrosopyrrolidine	930-55-2	10	330
155.	5-Nitro-o-toluidine	99-55-8	10	330
156.	Parathion	56-38-2	10	330
157.	Pentachlorobenzene	608-93-5	10	330
158.	Pentachlorodibenzo-p-dioxins (all isomers)		0.01	1.0
159.	Pentachlorodibenzofurans (all isomers)		0.01	1.0
160.	Pentachloronitrobenzene	82-68-8	10	330
161.	Pentachlorophenol	87-86-5	50	1,700
162.	Phenacetin	62-44-2	10	330
163.	Phenanthrene	85-01-8	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
F.	Appendix IX Substances (cont.)			
	Semivolatiles (cont.)			
164.	Phenol	108-95-2	10	330
165.	p-Phenylenediamine	106-50-3	10	330
166.	Pronamide	23950-58-5	10	330
167.	Pyrene	129-00-0	10	330
168.	Safrole	94-59-7	10	330
169.	1,2,4,5-Tetrachloro-benzene	95-94-3	10	330
170.	2,3,7,8-Tetrachloro-dibenzo-p-dioxin; (2,3,7,8-TCDD)	1746-01-6	0.005	0.5
171.	Tetrachlorodibenzo-p-dioxins (all isomers)		0.01	1.0
172.	Tetrachlorodibenzo-furans (all isomers)		0.01	1.0
173.	2,3,4,6-Tetrachloro-phenol	58-90-2	10	330
174.	Tetraethyldithiopyro-phosphate	3689-24-5	10	330
175.	o-Toluidine	95-53-4	10	330
176.	1,2,4-Trichloro-benzene	120-82-1	10	330
177.	2,4,5-Trichlorophenol	95-95-4	10	330
178.	2,4,6-Trichlorophenol	88-06-2	10	330
179.	O,O,O-Triethyl-phosphorothioate	126-68-1	10	330
180.	1,2,3-Trinitrobenzene	99-35-4	10	330
	Pesticides/Herbicides/PCBs			
181.	Aldrin	309-00-2	0.05	8.0
182.	AROCLOR-1016	12674-11-2	0.5	80
183.	AROCLOR-1221	11104-28-2	0.5	80
184.	AROCLOR-1232	11141-16-5	0.5	80
185.	AROCLOR-1242	53469-21-9	0.5	80
186.	AROCLOR-1248	12672-29-6	0.5	80
187.	AROCLOR-1254	11097-69-1	1.0	160

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

	Parameter	CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
F.	Appendix IX Substances (cont.)			
	Pesticides/Herbicides/PCBs (continued)			
188.	AROCLOR-1260	11096-82-5	1.0	160
189.	alpha-BHC	319-84-6	0.05	8.0
190.	beta-BHC	319-85-7	0.05	8.0
191.	delta-BHC	319-86-8	0.05	8.0
192.	gamma-BHC (Lindane)	58-89-9	0.05	8.0
193.	2-sec-Butyl-4,6-dinitrophenol; (Dinoseb; DNBP)	88-85-7	1.0	160
194.	Chlordane (Total)	57-74-9	0.5	80
195.	2,4-Dichlorophenoxy-acetic acid; (2,4-D)	94-75-7	10.	800
196.	4,4'-DDD	72-54-8	0.10	16
197.	4,4'-DDE	72-55-9	0.10	16
198.	4,4'-DDT	50-29-3	0.10	16
199.	Dieldrin	60-57-1	0.10	16
200.	Disulfoton	298-04-4	2.0	320
201.	Endosulfan I	959-98-8	0.10	16
202.	Endosulfan II	33213-65-9	0.10	16
203.	Endosulfan sulfate	1031-07-8	0.10	16
204.	Endrin	72-20-8	0.10	16
205.	Endrin aldehyde	7421-93-4	0.20	32
206.	Heptachlor	76-44-8	0.05	8.0
207.	Heptachlor epoxide	1024-57-3	0.05	8.0
208.	Methoxychlor	72-43-5	0.05	80
209.	Methyl parathion	298-00-0	0.5	80
210.	Phorate	298-02-2	2.0	320
211.	(2,4,5-Trichloro-phenoxy)propanoic acid; (2,4,5-TP; Silvex)	93-72-1	2.0	320
212.	2,4,5-Trichloro-phenoxyacetic acid (2,4,5-T)	93-76-5	2.0	320
213.	Toxaphene	8001-35-2	1.0	160

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
F.	Appendix IX Substances (cont.)			
	Inorganics			
214.	Antimony		60	6,000
215.	Arsenic		10	1,000
216.	Barium		200	20,000
217.	Beryllium		5.0	500
218.	Cadmium		5.0	500
219.	Chromium		10	1,000
220.	Cobalt		50	5,000
221.	Copper		25	2,500
222.	Cyanide	57-12-5	40	4,000
223.	Lead		5.0	500
224.	Mercury		0.2	20
225.	Nickel		40	4,000
226.	Selenium		5.0	500
227.	Silver		10	1,000
228.	Sulfide	18496-25-8	10,000	-
229.	Thallium		10	1,000
230.	Tin		40	4,000
231.	Vanadium		50	5,000
232.	Zinc		20	2,000
G.	Volatile Organics (Method 8240)			
1.	Acetone	67-64-1	10	10
2.	Benzene	71-43-2	10	10
3.	Bromodichloromethane	75-27-4	10	10
4.	Bromoform	75-25-2	10	10
5.	Bromomethane	74-83-9	10	10
6.	2-Butanone (Methyl ethyl ketone)	78-93-3	10	10
7.	Carbon disulfide	75-15-0	10	10
8.	Carbon tetrachloride	56-23-5	10	10
9.	Chlorobenzene	108-90-7	10	10
10.	Chloroethane	75-00-3	10	10
11.	2-Chloroethyl vinyl ether	110-75-8	10	10
12.	Chloroform	67-66-3	10	10
13.	Chloromethane	74-87-3	10	10
14.	Dibromochloromethane	124-48-1	10	10
15.	1,2-Dichlorobenzene	95-50-1	10	10

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
G.	Volatile Organics (Method 8240) (cont.)			
16.	1,3-Dichlorobenzene	541-73-1	10	10
17.	1,4-Dichlorobenzene	106-46-7	10	10
18.	1,1-Dichloroethane	75-34-3	10	10
19.	1,2-Dichloroethane	107-06-2	10	10
20.	1,1-Dichloroethene	75-35-4	10	10
21.	1,2-Dichloroethene (Total)	540-59-0	10	10
22.	Dichloromethane	75-09-2	10	10
23.	1,2-Dichloropropane	78-87-5	10	10
24.	cis-1,3-Dichloro-propene	10061-01-5	10	10
25.	trans-1,3-Dichloro-propene	10061-02-6	10	10
26.	Ethylbenzene	100-41-4	10	10
27.	2-Hexanone	591-78-6	10	10
28.	4-Methyl-2-pentanone (Methyl iso-butyl ketone)	108-10-1	10	10
29.	Styrene	100-42-5	10	10
30.	1,1,2,2-Tetrachloro-ethane	79-34-5	10	10
31.	Tetrachloroethylene	127-18-4	10	10
32.	Toluene	108-88-3	10	10
33.	1,1,1-Trichloroethane	71-55-6	10	10
34.	1,1,2-Trichloroethane	79-00-5	10	10
35.	Trichloroethene	79-01-6	10	10
36.	Vinyl acetate	108-05-4	10	10
37.	Vinyl chloride	75-01-4	10	10
38.	Xylenes (Total)	1330-20-7	10	10
The Following Volatile Organics May Also Be Analysed For Using Method 8240				
1.	Acetonitrile	75-05-8	100	100
2.	Acrolein	107-02-8	100	100
3.	Acrylonitrile	107-13-1	100	100
4.	Allyl alcohol	107-18-6	100	100
5.	Allyl chloride (3-Chloropropene)	107-05-1	10	10
6.	Benzyl chloride	100-44-7	100	100
7.	Bromoactone	598-31-2	100	100
8.	Bromochlormethane	74-97-5	10	10
9.	2-Chloroethanol	107-07-3	100	100

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
G.	Volatile Organics (Method 8240) (supplemental list continued)			
10.	Cloroprene (2-Chloro-1,3-butadiene)	126-99-8	10	10
11.	3-Chloropropionitrile	542-76-7	100	100
12.	1,2-Dibromo-3-chloro-propane	96-12-8	100	100
13.	1,2-Dibromoethane	106-93-4	10	10
14.	Dibromomethane	74-95-3	10	10
15.	1,4-Dichloro-2-butene	110-57-6	100	100
16.	Dichlorodifluoromethane	75-71-8	10	10
17.	1,3-Dichloro-2-propanol	96-23-1	100	100
18.	1,2,3,4-Diepoxybutane	1464-53-5	100	100
19.	1,4-Dioxane	123-91-1	100	100
20.	Epichlorohydrin	106-89-8	100	100
21.	Ethanol	64-17-5	100	100
22.	Ethylene oxide	75-21-8	100	100
23.	Ethylmethacrylate	97-63-2	10	10
24.	2-Hydroxypropionitrile	591-78-6	100	100
25.	Iodomethane (Methyl iodide)	74-88-4	10	10
26.	Isobutyl alcohol (2-Methyl-1-propanol)	78-83-1	100	100
27.	Malononitrile	126-98-7	100	100
28.	Methacrylonitrile	126-98-7	100	100
29.	Methylmethacrylate	80-62-6	10	10
30.	Pentachloroethane	76-01-7	10	10
31.	2-Picoline	109-06-8	100	100
32.	Propargyl alcohol	107-19-7	100	100
33.	β-Propiolacetone	57-57-8	100	100
34.	Propionitrile	107-12-0	100	100
35.	n-Propylamine	107-10-8	100	100
36.	Pyridine	110-86-1	100	100
37.	1,1,1,2-Tetrachloroethane	630-20-6	10	10
38.	Trichlorofluoromethane	75-69-4	10	10
39.	1,2,3-Trichloropropane	96-18-4	10	10

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
H.	Low Concentration Volatile Organics (Method 8260)			
1.	Acetone	67-64-1	5	10
2.	Acrylonitrile	107-13-1	10	100
3.	Benzene	71-43-2	1	10
4.	Bromochlormethane	74-97-5	1	10
5.	Bromodichloromethane	75-27-4	1	10
6.	Bromoform	75-25-2	1	10
7.	Bromomethane (Methyl bromide)	74-83-9	1	10
8.	2-Butanone (Methyl ethyl ketone)	78-93-3	5	10
9.	Carbon disulfide	75-15-0	1	10
10.	Carbon tetrachloride	56-23-5	1	10
11.	Chlorobenzene	108-90-7	1	10
12.	Chloroethane	75-00-3	1	10
13.	2-Chloroethyl vinyl ether	110-75-8	1	10
14.	Chloroform	67-66-3	1	10
15.	Chloromethane (Methyl chloride)	74-87-3	1	10
16.	Dibromochloromethane	124-48-1	1	10
17.	1,2-Dibromo-3-chloro-propane	96-12-8	1	100
18.	1,2-Dibromoethane	106-93-4	1	10
19.	1,2-Dichlorobenzene	95-50-1	1	10
20.	1,3-Dichlorobenzene	541-73-1	1	10
21.	1,4-Dichlorobenzene	106-46-7	1	10
22.	trans-1,4-Dichloro-2-butene	110-57-6	1	100
23.	1,1-Dichloroethane	75-34-3	1	10
24.	1,2-Dichloroethane	107-06-2	1	10
25.	1,1-Dichloroethene	75-35-4	1	10
26.	cis-1,2-Dichloroethene	156-59-2	1	10
27.	trans-1,2-Dichloroethene	156-60-5	1	10
28.	Dichloromethane (Methylene chloride)	75-09-2	2	10
29.	1,2-Dichloropropane	78-87-5	1	10
30.	cis-1,3-Dichloro-propene	10061-01-5	1	10
31.	trans-1,3-Dichloro-propene	10061-02-6	1	10
32.	Ethylbenzene	100-41-4	1	10
33.	2-Hexanone	591-78-6	5	10

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter	CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
H. Low Concentration Volatile Organics (Method 8260) (continued)			
34. Iodomethane (Methyl iodide)	74-88-4	1	10
35. 4-Methyl-2-pentanone (Methyl iso-butyl ketone)	108-10-1	5	10
36. Styrene	100-42-5	1	10
37. 1,1,1,2-Tetrachloroethane	630-20-6	1	10
38. 1,1,2,2-Tetrachloroethane	79-34-5	1	10
39. Tetrachloroethene	127-18-4	1	10
40. Toluene	108-88-3	1	10
41. 1,1,1-Trichloroethane	71-55-6	1	10
42. 1,1,2-Trichloroethane	79-00-5	1	10
43. Trichloroethene	79-01-6	1	10
44. Trichlorofluoromethane	75-69-4	1	10
45. 1,2,3-Trichloropropane	96-18-4	1	10
46. Vinyl acetate	108-05-4	1	10
47. Vinyl chloride	75-01-4	1	10
48. Xylenes (Total)	1330-20-7	1	10
The Following Volatile Organics May Also Be Analysed For Using Method 8260			
1. Acetonitrile	75-05-8	100	100
2. Acrolein	107-02-8	100	100
5. Allyl chloride (3-Chloropropene)	107-05-1	10	10
3. Bromobenzene	108-86-1	1	10
4. n-Butylbenzene	104-51-8	1	10
5. sec-Butylbenzene	135-98-8	1	10
6. tert-Butylbenzene	98-06-6	1	10
7. Cloroprene (2-Chloro-1,3-butadiene)	126-99-8	10	10
8. 2-Chlorotoluene	95-49-8	1	10
9. 4-Chlorotoluene	106-43-4	1	10
10. Dibromomethane	74-95-3	1	10
11. Dichlorodifluoromethane	75-71-8	1	10
12. 1,3-Dichloropropane	142-28-9	1	10
13. 2,2-Dichloropropane	594-20-7	1	10
14. 1,1-Dichloropropene	563-58-6	1	10
15. Ethylmethacrylate	97-63-2	10	10
16. Hexachlorobutadiene	87-68-3	1	10
17. Hexachloroethane	67-72-1	1	10

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
H.	Low Concentration Volatile Organics (Method 8260) (supplemental list continued)			
18.	Isobutyl alcohol (2-Methyl-1-propanol)	78-83-1	100	100
19.	Isodrin	465-73-6	10	10
20.	Isopropylbenzene	98-82-8	1	10
21.	p-Isopropyltoluene	99-87-6	1	10
22.	Methacrylonitrile	126-98-7	100	100
23.	Methylmethacrylate	80-62-6	10	10
24.	Naphthalene	91-20-3	1	10
25.	Propionitrile	107-12-0	100	100
18.	n-Propylbenzene	103-65-1	1	10
19.	1,2,3-Trichlorobenzene	87-61-6	1	10
20.	1,2,4-Trichlorobenzene	120-82-1	1	10
21.	1,2,4-Trimethylbenzene	95-63-6	1	10
22.	1,3,5-Trimethylbenzene	108-67-8	1	10
I.	Semivolatile Organics (Method 8270)			
1.	Acenaphthene	83-32-9	10	330
2.	Acenaphthylene	208-96-8	10	330
3.	Anthracene	120-12-7	10	330
4.	Benz[a]anthracene	56-55-3	10	330
5.	Benzo[b]fluoranthene	205-99-2	10	330
6.	Benzo[k]fluoranthene	207-08-9	10	330
7.	Benzo[g.h,i]perylene	191-24-2	10	330
8.	Benzo[a]pyrene	50-32-8	10	330
9.	Benzyl alcohol	100-51-6	10	330
10.	Benzyl butyl phthalate	85-68-7	10	330
11.	Bis(2-chloroethoxy)-methane	111-91-1	10	330
12.	Bis(2-chloroethyl)ether	111-44-4	10	330
13.	Bis(2-ethylhexyl)-phthalate	117-81-7	10	330
14.	4-Bromophenyl phenyl ether	101-55-3	10	330
15.	4-Chloroaniline	106-47-8	10	330
16.	4-Chloro-3-methylphenol (p-Chloro-m-cresol)	59-50-7	10	330
17.	2-Chloronaphthalene	91-58-7	10	330
18.	2-Chlorophenol	95-57-8	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
I.	Semivolatile Organics (Method 8270) (continued)			
19.	4-Chlorophenyl phenyl ether	7005-72-3	10	330
20.	Chrysene	218-01-9	10	330
21.	Dibenz[a,h]anthracene	53-70-3	10	330
22.	Dibenzofuran	132-64-9	10	330
23.	Di-n-butyl phthalate	84-74-2	10	330
24.	1,2-Dichlorobenzene	95-50-1	10	330
25.	1,3-Dichlorobenzene	541-73-1	10	330
26.	1,4-Dichlorobenzene	106-46-7	10	330
27.	3,3'-Dichlorobenzidine	91-94-1	20	660
28.	2,4-Dichlorophenol	120-83-2	10	330
29.	Diethyl phthlate	84-66-2	10	330
30.	2,4-Dimethylphenol	105-67-9	10	330
31.	Dimethyl phthlate	131-11-3	10	330
32.	4,6-Dinitro-2-methyl-phenol	534-52-1	25	800
33.	2,4-Dinitrophenol	51-28-5	25	800
34.	2,4-Dinitrotoluene	121-14-2	10	330
35.	2,6-Dinitrotoluene	606-20-2	10	330
36.	Di-n-octylphthalate	117-84-0	10	330
37.	Fluoranthene	206-44-0	10	330
38.	Fluorene	86-73-7	10	330
39.	Hexachlorobenzene	118-74-1	10	330
40.	Hexachlorobutadiene	87-68-3	10	330
41.	Hexachlorocyclo-pentadiene	77-47-4	10	330
42.	Hexachloroethane	67-72-1	10	330
43.	Indeno[1,2,3-c,d]-pyrene	193-39-5	10	330
44.	Isophorone	78-59-1	10	330
45.	2-Methylnaphthalene	91-57-6	10	330
46.	2-Methylphenol (o-Cresol)	95-48-7	10	330
47.	4-Methylphenol (p-Cresol)	106-44-5	10	330
48.	Naphthalene	91-20-3	10	330
49.	2-Nitroaniline	88-74-4	25	800
50.	3-Nitroaniline	99-09-2	25	800
51.	4-Nitroaniline	100-01-6	25	800
52.	Nitrobenzene	98-95-3	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
I.	Semivolatile Organics (Method 8270) (continued)			
53.	2-Nitrophenol	88-75-5	10	330
54.	4-Nitrophenol	100-02-7	25	800
55.	N-Nitrosodimethylamine	62-75-9	10	330
56.	N-Nitrosodiphenylamine	86-30-6	10	330
57.	N-Nitrosodi-n-propyl-amine	621-24-7	10	330
58.	2,2'-oxybis(1-Chloropropane (Bis(2-chloroisopropyl)ether)	108-60-1	10	330
59.	Pentachlorophenol	87-86-5	25	800
60.	Phenanthrene	85-01-8	10	330
61.	Phenol	108-95-2	10	330
62.	Pyrene	129-00-0	10	330
63.	1,2,4-Trichlorobenzene	120-82-1	10	330
64.	2,4,5-Trichlorophenol	95-95-4	10	330
65.	2,4,6-Trichlorophenol	88-06-2	10	330
The Following Semivolatile Organics May Also Be Analysed For Using Method 8270				
1.	Acetophenone	98-86-2	10	330
2.	2-Acetylaminofluorene (2-AAF)	53-96-3	20	660
3.	Acetyl-2-thiourea	591-08-2	1,000	33,000
4.	2-Aminoanthraquinone	117-79-3	20	660
5.	Aminoazobenzene	60-09-3	10	330
6.	4-Aminobiphenyl	92-67-1	20	660
7.	Anilazine	101-05-3	100	3,300
8.	Aniline	62-53-3	10	330
9.	o-Anisidine	90-04-0	10	330
10.	Aramite	140-57-8	20	660
11.	Azinphos methyl	86-50-0	100	3,300
12.	Barban	101-27-9	200	6,600
13.	Benzidine	92-87-5	1,000	33,000
14.	Benzoic Acid	65-85-0	50	1,700
15.	p-Benzoquinone	106-51-4	10	330
16.	Bromoxynil	1689-84-5	10	330
17.	Captafol	2425-06-1	20	660
18.	Captan	133-06-2	50	1,700
19.	Carbaryl	63-25-2	10	330
20.	Carbazole	86-74-8	10	330
21.	Carbofuran	1563-66-2	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
I.	Semivolatile Organics (Method 8270) (supplemental list continued)			
22.	Carbophenothion	786-19-6	10	330
23.	Chlorfenvinphos	470-90-6	20	660
24.	Chlorobenzilate	510-15-6	10	330
25.	5-Chloro-2-methylaniline	95-79-4	10	330
26.	3-(Chloromethyl)pyridine hydrochloride	6959-48-4	100	3,300
27.	1-Chloronaphthalene	90-13-1	10	330
28.	Coumaphos	56-72-4	40	1,300
29.	p-Cresidine	120-71-8	10	330
30.	Crotoxyphos	7700-17-6	20	660
31.	2-Cyclohexyl-4,6-dinitrophenol	131-89-5	100	3,300
32.	Demeton-O	298-03-3	10	330
33.	Demeton-S	2303-16-4	10	330
34.	Diallate	2303-16-4	10	330
35.	2,4-Diaminotoluene	95-80-7	20	660
36.	Dibenz[a,j]acridine	224-42-0	10	330
37.	Dibenzo[a,e]pyrene	192-65-4	10	330
38.	Dichlone	117-80-6	100	3,300
39.	2,6-Dichlorophenol	87-65-0	10	330
40.	Dichlorovos	62-73-7	10	330
41.	Dicrotophos	141-66-2	10	330
42.	Diethylstilbestrol	56-53-1	20	660
43.	O,O-Diethyl-0-2-pyrazinyl-phosphoro-thioate	297-97-2	10	330
44.	Diethyl sulfate	64-67-5	100	3,300
45.	Dimethoate	60-51-5	10	330
46.	3,3'-Dimethoxybenzidine	119-90-4	100	3,300
47.	p-(Dimethylamino)azo-benzene	60-11-7	10	330
48.	7,12-Dimethylbenz[a]-anthracene	57-97-6	10	330
49.	3,3'-Dimethylbenzidine	119-93-7	10	330
50.	α,α-Dimethylphen-ethylamine	122-09-8	10	330
51.	1,2-Dinotrobenzene	528-29-0	40	1,300
52.	1,3-Dinitrobenzene	99-65-0	20	660
53.	1,4-Dintrobenzene	100-25-4	40	1,300
54.	Dinocap	39300-45-3	100	3,300

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
I.	Semivolatile Organics (Method 8270) (supplemental list continued)			
55.	Dinoseb	88-85-7	20	660
56.	Diphenylamine	122-39-4	10	330
57.	5,5-Diphenylhydantoin	57-41-0	20	660
58.	1,2-Diphenylhydrazine	122-66-7	100	3,300
59.	Disulfoton	298-04-4	10	330
60.	Ethion	563-12-2	10	330
61.	Ethoxy-4-nitrophenoxypheny-phosphine sulfide (EPN)	2104-64-5	10	330
62.	Ethyl carbamate	51-79-6	50	1,700
63.	Ethyl methanesulfonate	62-50-0	20	660
64.	Famphur	52-85-7	20	660
65.	Fensulfothion	115-90-2	40	1,300
66.	Fenthion	55-38-9	10	330
67.	Fluchloralin	33245-39-5	20	660
68.	Hexachlorophene	70-30-4	50	1,700
69.	Hexachloropropene	1888-71-7	10	330
70.	Hexamethylphosphoramide	680-31-9	20	660
71.	Hydroquinone	123-31-9	100	3,300
72.	Isodrin	465-73-6	20	660
73.	Isosafrole	120-58-1	10	330
74.	Kepone	143-50-0	20	660
75.	Leptophos	21609-90-5	10	330
76.	Malathion	121-75-5	50	1,700
77.	Maleic anhydride	108-31-6	100	3,300
78.	Mestranol	72-33-3	20	660
79.	Methapyrilene	91-80-5	100	3,300
80.	3-Methylcholanthrene	56-49-5	10	330
81.	4,4'-Methylenebis(2-chloro-aniline)	101-14-4	100	3,300
82.	Methyl methanesulfonate	66-27-3	10	330
83.	Methyl parathion	298-00-0	10	330
84.	3-Methylphenol (m-Cresol)	108-39-4	10	330
85.	Mevinphos	7786-34-7	10	330
86.	Mexacarbate	315-18-4	20	660
87.	Monocrotophos	6923-22-4	40	1,300
88.	Naled	300-76-5	20	660
89.	1,4-Naphthoquinone	130-15-4	10	330
90.	1-Naphthylamine	134-32-7	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
I.	Semivolatile Organics (8270) (supplemental list continued)			
91.	2-Naphthylamine	91-59-8	10	330
92.	Nicotine	54-11-5	20	660
93.	5-Nitroacenaphthene	602-87-9	10	330
94.	5-Nitro-o-anisidine	99-59-2	10	330
95.	4-Nitrobiphenyl	92-93-3	10	330
96.	Nitrofen	1836-75-5	20	660
97.	4-Nitroquinoline-1-oxide	56-57-5	40	1,300
98.	N-Nitrosodi-n-butyl-amine	924-16-3	10	330
99.	N-Nitrosodiethylamine	55-18-5	20	660
100.	N-Nitrosomethylethyl-amine	10595-95-6	10	330
101.	N-Nitrosomorpholine	59-89-2	10	330
102.	N-Nitrosopiperidine	100-75-4	20	660
103.	N-Nitrosopyrrolidine	930-55-2	40	1,300
104.	5-Nitro-o-toluidine	99-55-8	10	330
105.	Octamethyl pyrophos-phoramide	152-16-9	200	6,600
106.	4,4'-Oxydianiline	101-80-4	20	660
107.	Parathion	56-38-2	10	330
108.	Pentachlorobenzene	608-93-5	10	330
109.	Pentachloronitrobenzene	82-68-8	20	660
110.	Phenacetin	62-44-2	20	660
111.	Phenobarbital	50-06-6	10	330
112.	p-Phenylenediamine	106-50-3	10	330
113.	Phorate	298-02-2	10	330
114.	Phosalone	2310-17-0	100	3,300
115.	Phosmet	732-11-6	40	1,300
116.	Phosphamidon	13171-21-6	100	3,300
117.	Phthalic anhydride	85-44-9	100	3,300
118.	2-Picoline	109-06-8	100	3,300
119.	Piperonyl sulfoxide	120-62-7	100	3,300
120.	Pronamide	23950-58-5	10	330
121.	Propylthiouracil	51-52-5	100	3,300
122.	Pyridine	110-86-1	100	3,300
123.	Resorcinol	108-46-3	100	3,300
124.	Safrole	94-59-7	10	330
125.	Strychnine	60-41-3	40	1,300
126.	Sulfallate	95-06-7	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
I.	Semivolatile Organics (8270) (supplemental list continued)			
127.	Terbufos	13071-79-9	20	660
128.	1,2,4,5-Tetrachloro-benzene	95-94-3	10	330
129.	2,3,4,6-Tetrachloro-phenol	58-90-2	10	330
130.	Tetrachlorvinphos (Stirophos)	961-11-5	20	660
131.	Tetraethyldithiopyro-phosphate	3689-24-5	10	330
132.	Tetraethyl pyrophosphate	107-49-3	40	1,300
133.	Thionazine	297-97-2	20	660
134.	Thiophenol (Benzenethiol)	108-98-5	20	660
135.	Toluene diisocyanate	584-84-9	100	3,300
136.	o-Toluidine	95-53-4	10	330
137.	Trifluralin	1582-09-8	10	330
138.	2,4,5-Trimethylaniline	137-17-7	10	330
139.	Trimethyl phosphate	512-56-1	10	330
140.	O,O,O-Triethyl-phosphorothioate	126-68-1	10	330
141.	1,2,3-Trinitrobenzene	99-35-4	10	330
142.	Tris(2,3-dibromopropyl) phosphate	126-72-7	200	6,600
143.	Tri-p-tolyl phosphate	78-32-0	10	330

RCRA Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter		CAS Number	Contract Required Quantitation Limits Low Water (µg/L)	Low Soil/Sediments (µg/Kg)
J.	Pesticides/Aroclors (Method 8080)			
1.	Aldrin	309-00-2	0.05	8.0
2.	AROCLOR-1016	12674-11-2	0.5	80
3.	AROCLOR-1221	11104-28-2	0.5	80
4.	AROCLOR-1232	11141-16-5	0.5	80
5.	AROCLOR-1242	53469-21-9	0.5	80
6.	AROCLOR-1248	12672-29-6	0.5	80
7.	AROCLOR-1254	11097-69-1	1.0	160
8.	AROCLOR-1260	11096-82-5	1.0	160
9.	alpha-BHC	319-84-6	0.05	8.0
10.	beta-BHC	319-85-7	0.05	8.0
11.	delta-BHC	319-86-8	0.05	8.0
12.	gamma-BHC (Lindane)	58-89-9	0.05	8.0
13.	Chlordane (Total)	57-74-9	0.5	80
14.	4,4'-DDD	72-54-8	0.10	16
15.	4,4'-DDE	72-55-9	0.10	16
16.	4,4'-DDT	50-29-3	0.10	16
17.	Dieldrin	60-57-1	0.10	16
18.	Endosulfan I	959-98-8	0.10	16
19.	Endosulfan II	33213-65-9	0.10	16
20.	Endosulfan sulfate	1031-07-8	0.10	16
21.	Endrin	72-20-8	0.10	16
22.	Endrin aldehyde	7421-93-4	0.20	32
23.	Heptachlor	76-44-8	0.05	8.0
24.	Heptachlor epoxide	1024-57-3	0.05	8.0
25.	Methoxychlor	72-43-5	0.05	80
26.	Toxaphene	8001-35-2	1.0	160

Section IV -- Superfund-CLP Low Concentration Organics

Superfund-CLP Low Concentration Organics
Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)

	Volatiles	CAS Number	Quantitation Limits* Low Water µg/L
1.	Chloromethane	74-87-3	1
2.	Bromomethane	74-83-9	1
3.	Vinyl chloride	75-01-4	1
4.	Chloroethane	75-00-3	1
5.	Methylene chloride	75-09-2	2
6.	Acetone	67-64-1	5
7.	Carbon Disulfide	75-15-0	1
8.	1,1-Dichloroethene	75-35-4	1
9.	1,1-Dichloroethane	75-35-3	1
10.	cis-1,2-Dichloroethene	156-59-4	1
11.	trans-1,2-Dichloroethene	156-60-5	1
12.	Chloroform	67-66-3	1
13.	1,2-Dichloroethane	107-06-2	1
14.	2-Butanone	78-93-3	5
15.	Bromochloromethane	74-97-5	1
16.	1,1,1-Trichloroethane	71-55-6	1
17.	Carbon tetrachloride	56-23-5	1
18.	Bromodichloromethane	75-27-4	1
19.	1,2-Dichloropropane	78-87-5	1
20.	cis-1,3-Dichloropropene	10061-01-5	1
21.	Trichloroethene	79-01-6	1
22.	Dibromochloromethane	124-48-1	1
23.	1,1,2-Trichloroethane	79-00-5	1
24.	Benzene	71-43-2	1
25.	trans-1,3-Dichloropropene	10061-02-6	1
26.	Bromoform	75-25-2	1
27.	4-Methyl-2-pentanone	108-10-1	5
28.	2-Hexanone	591-78-6	5
29.	Tetrachloroethene	127-18-4	1
30.	1,1,2,2-Tetrachloroethane	79-34-5	1

Superfund-CLP Low Concentration Organics
Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)

	Volatiles (cont.)	Low CAS Number	Quantitation Limits* Water µg/L	
31.	1,2-Dibromoethane		106-93-4	1
32.	Toluene		108-88-3	1
33.	Chlorobenzene		108-90-7	1
34.	Ethyl Benzene		100-41-4	1
35.	Styrene		100-42-5	1
36.	o/p-Xylene		95-47-6/106-42-3	1
37.	m-Xylene		108-38-3	1
38.	1,3-Dichlorobenzene		541-73-1	1
39.	1,4-Dichlorobenzene		106-46-7	1
40.	1,2-Dichlorobenzene		95-50-1	1
41.	1,2-Dibromo-3-chloropropane		96-12-8	1
42.	Vinyl acetate		108-05-4	1

Superfund-CLP Low Concentration Organics
Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)

	Semivolatiles	Low CAS Number	Quantitation Limits* Water µg/L
1.	Phenol	108-95-2	5
2.	bis(2-Chloroethyl) ether	111-44-4	5
3.	2-Chlorophenol	95-57-8	5
4.	2-Methylphenol	95-48-7	5
5.	2,2'-oxybis(1-Chloro-propane) #	108-60-1	5
6.	4-Methylphenol	106-44-5	5
7.	N-Nitroso-di-n-propylamine	621-64-7	5
8.	Hexachloroethane	67-72-1	5
9.	Nitrobenzene	98-95-3	5
10.	Isophorone	78-59-1	5
11.	2-Nitrophenol	88-75-5	5
12.	2,4-Dimethylphenol	105-67-9	5
13.	bis(2-Chloroethoxy) methane	111-91-1	5
14.	2,4-Dichlorophenol	120-83-2	5
15.	1,2,4-Trichlorobenzene	120-82-1	5
16.	Naphthalene	91-20-3	5
17.	4-Chloroaniline	106-47-8	5
18.	Hexachlorobutadiene	87-68-3	5
19.	4-Chloro-3-methylphenol	59-50-7	5
20.	2-Methylnaphthalene	91-57-6	5
21.	Hexachlorocyclopentadiene	77-47-4	5
22.	2,4,6-Trichlorophenol	88-06-2	5
23.	2,4,5-Trichlorophenol	95-95-4	20
24.	2-Chloronaphthalene	91-58-7	5
25.	2-Nitroaniline	88-74-4	20
26.	Dimethyl phthalate	131-11-3	5
27.	Acenaphthylene	208-96-8	5
28.	2,6-Dinitrotoluene	606-20-2	5
29.	3-Nitroaniline	99-09-2	20
30.	Acenaphthene	83-32-9	5

Previously known by the name bis(2-Chloroisopropyl) ether

Superfund-CLP Low Concentration Organics
Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)

	Semivolatiles (cont.)	Low CAS Number	Quantitation Limits* Water µg/L	
31.	2,4-Dinitrophenol		51-28-5	20
32.	4-Nitrophenol		100-02-7	20
33.	Dibenzofuran		132-64-9	5
34.	2,4-Dinitrotoluene		121-14-2	5
35.	Diethylphthalate		84-66-2	5
36.	4-Chlorophenyl phenyl ether		7005-72-3	5
37.	Fluorene		86-73-7	5
38.	4-Nitroaniline		100-01-6	20
39.	4,6-Dinitro-2-methylphenol		534-52-1	20
40.	N-nitrosodiphenylamine		86-30-6	5
41.	4-Bromophenyl phenyl ether		101-55-3	5
42.	Hexachlorobenzene		118-74-1	5
43.	Pentachlorophenol		87-86-5	20
44.	Phenanthrene		85-01-8	5
45.	Anthracene		120-12-7	5
46.	Di-n-butyl phthalate		84-74-2	5
47.	Fluoranthene		206-44-0	5
48.	Pyrene		129-00-0	5
49.	Butyl benzyl phthalate		85-68-7	5
50.	3,3'-Dichlorobenzidine		91-94-1	5
51.	Benz[a]anthracene		56-55-3	5
52.	Chrysene		218-01-9	5
53.	bis(2-Ethylhexyl)phthalate		117-81-7	5
54.	Di-n-octyl phthalate		117-84-0	5
55.	Benzo[b]fluoranthene		205-99-2	5
56.	Benzo[k]fluoranthene		207-08-9	5
57.	Benzo[a]pyrene		50-32-8	5
58.	Indeno[1,2,3-cd]pyrene		193-39-5	5
59.	Dibenz[a,h]anthracene		53-70-3	5
60.	Benzo[g,h,i]perylene		191-24-2	5

Superfund-CLP Low Concentration Organics
Target Compound List (TCL) and
Contract Required Quantitation Limits (CRQL)

	Pesticides/Aroclors	Low CAS Number	Quantitation Limits* Water µg/L
1.	alpha-BHC	319-84-6	0.01
2.	beta-BHC	319-85-7	0.01
3.	delta-BHC	319-86-8	0.01
4.	gamma-BHC (Lindane)	58-89-9	0.01
5.	Heptachlor	76-44-8	0.01
6.	Aldrin	309-00-2	0.01
7.	Heptachlor epoxide	1024-57-3	0.01
8.	Endosulfan I	959-98-8	0.01
9.	Dieldrin	60-57-1	0.02
10.	4,4'-DDE	72-55-9	0.02
11.	Endrin	72-20-8	0.02
12.	Endosulfan II	33213-65-9	0.02
13.	4,4'-DDD	72-54-8	0.02
14.	Endosulfan sulfate	1031-07-8	0.02
15.	4,4'-DDT	50-29-3	0.02
16.	Methoxychlor	72-43-5	0.10
17.	Endrin ketone	53494-70-5	0.02
18.	Endrin aldehyde	7421-36-3	0.02
19.	alpha-Chlordane	5103-71-9	0.01
20.	gamma-Chlordane	5103-74-2	0.01
21.	Toxaphene	8001-35-2	1.0
22.	AROCLOR-1016	12674-11-2	0.20
23.	AROCLOR-1221	11104-28-2	0.20
24.	AROCLOR-1232	11141-16-5	0.40
25.	AROCLOR-1242	53469-21-9	0.20
26.	AROCLOR-1248	12672-29-6	0.20
27.	AROCLOR-1254	11097-69-1	0.20
28.	AROCLOR-1260	11096-82-5	0.20

Section V -- NYSDEC Division Of Solid and Hazardous Materials
6 NYCRR Part 360 Parameters

6 NYCRR Part 360 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit

Parameter	CAS Number	Contract Required Quantitation Level (µg/L)
Routine Parameters		
Leachate Indicators:		
1. Total Kjeldahl Nitrogen, as N		60
2. Ammonia, as N		50
3. Nitrate-Nitrite		100
4. Chemical Oxygen Demand (COD)		1,000
5. Biochemical Oxygen Demand (BOD_5)		2,000
6. Total Organic Carbon		2,000
7. Total Dissolved Solids (TDS)		10,000
8. Sulfate		5,000
9. Total Alkalinity as $CaCO_3$		6,000
10. Total Phenols		10
11. Chloride		5,000
12. Bromide		2,000
13. Total Hardness as $CaCO_3$		20,000
Inorganic Parameters:		
1. Cadmium, Total		5
2. Calcium, Total		40
3. Iron, Total		100
4. Lead, Total		5
5. Magnesium, Total		5
6. Manganese, Total		15
7. Potassium, Total		40
8. Sodium, Total		10

6 NYCRR Part 360 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit (Continued)

Parameter	CAS Number	Contract Required Quantitation Level (µg/L)
Baseline Parameters		
Leachate Indicators:		
1. Total Kjeldahl Nitrogen, as N		60
2. Ammonia, as N		50
3. Nitrate-Nitrite		100
4. Chemical Oxygen Demand (COD)		1,000
5. Biochemical Oxygen Demand (BOD_5)		2,000
6. Total Organic Carbon		2,000
7. Total Dissolved Solids (TDS)		10,000
8. Sulfate		5,000
9. Total Alkalinity as $CaCO_3$		6,000
10. Total Phenols		10
11. Chloride		5,000
12. Bromide		2,000
13. Total Hardness as $CaCO_3$		20,000
14. Color		80
15. Boron	7440-42-8	20
Inorganic Parameters:		
1. Aluminum, Total		10
2. Antimony, Total		30
3. Arsenic, Total		10
4. Barium, Total		20
5. Beryllium, Total		5
6. Cadmium, Total		5
7. Calcium, Total		40
8. Chromium, Total		10
9. Chromium,Hexavalent	18540-29-9	30
10. Cobalt, Total		10
11. Copper, Total		10
12. Cyanide, Total		10
13. Iron, Total		100
14. Lead, Total		5
15. Magnesium, Total		5
16. Manganese, Total		15
17. Mercury, Total		0.2
18. Nickel, Total		40
19. Potassium, Total		40
20. Selenium, Total		5
21. Silver, Total		10
22. Sodium, Total		10

6 NYCRR Part 360 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit (Continued)

Parameter	CAS Number	Contract Required Quantitation Level (µg/L)
	Baseline Parameters (Continued)	
Inorganic Parameters (continued):		
23. Thallium, Total		10
24. Vanadium, Total		40
25. Zinc, Total		20
Organic Parameters:		
1. Acetone	67-64-1	5
2. Acrylonitrile	107-13-1	10
3. Benzene	71-43-2	1
4. Bromochlormethane	74-97-5	1
5. Bromodichloromethane	75-27-4	1
6. Bromoform	75-25-2	1
7. Bromomethane	74-83-9	1
8. 2-Butanone	78-93-3	5
9. Carbon disulfide	75-15-0	1
10. Carbon tetrachloride	56-23-5	1
11. Chlorobenzene	108-90-7	1
12. Chloroethane	75-00-3	1
13. Chloroform	67-66-3	1
14. Chloromethane	74-87-3	1
15. Dibromochloromethane	124-48-1	1
16. 1,2-Dibromo-3-chloro-propane	96-12-8	1
17. 1,2-Dibromoethane	106-93-4	1
18. 1,2-Dichlorobenzene	95-50-1	1
19. 1,3-Dichlorobenzene	541-73-1	1
20. 1,4-Dichlorobenzene	106-46-7	1
21. trans-1,4-Dichloro-2-butene	110-57-6	10
22. 1,1-Dichloroethane	75-34-3	1
23. 1,2-Dichloroethane	107-06-2	1
24. 1,1-Dichloroethene	75-35-4	1
25. cis-1,2-Dichloroethene	156-59-2	1
26. trans-1,2-Dichloroethene	156-60-5	1
27. Dichloromethane (Methylene chloride)	75-09-2	2
28. 1,2-Dichloropropane	78-87-5	1
29. cis-1,3-Dichloro-propene	10061-01-5	1
30. trans-1,3-Dichloro-propene	10061-02-6	1
31. Ethylbenzene	100-41-4	1

6 NYCRR Part 360 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit (Continued)

Parameter		CAS Number	Contract Required Quantitation Level (µg/L)
	Baseline Parameters (Continued)		
Organic Parameters (Continued):			
32.	2-Hexanone	591-78-6	5
33.	Iodomethane	74-88-4	1
34.	4-Methyl-2-pentanone	108-10-1	5
35.	Styrene	100-42-5	1
36.	1,1,1,2-Tetrachloroethane	630-20-6	1
37.	1,1,2,2-Tetrachloroethane	79-34-5	1
38.	Tetrachloroethene	127-18-4	1
39.	Toluene	108-88-3	1
40.	1,1,1-Trichloroethane	71-55-6	1
41.	1,1,2-Trichloroethane	79-00-5	1
42.	Trichloroethene	79-01-6	1
43.	Trichlorofluoromethane	75-69-4	1
44.	1,2,3-Trichloropropane	96-18-4	1
45.	Vinyl acetate	108-05-4	1
46.	Vinyl chloride	75-01-4	1
47.	Xylenes (Total)	1330-20-7	1

6 NYCRR Part 360 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit (Continued)

Parameter	CAS Number	Contract Required Quantitation Level (µg/L)
	Expanded Parameters	
Leachate Indicators:		
1. Total Kjeldahl Nitrogen, as N		60
2. Ammonia, as N		50
3. Nitrate-Nitrite		100
4. Chemical Oxygen Demand (COD)		1,000
5. Biochemical Oxygen Demand (BOD_5)		2,000
6. Total Organic Carbon		2,000
7. Total Dissolved Solids (TDS)		10,000
8. Sulfate		5,000
9. Total Alkalinity as $CaCO_3$		6,000
10. Total Phenols		10
11. Chloride		5,000
12. Bromide		2,000
13. Total Hardness as $CaCO_3$		20,000
14. Color		80
15. Boron	7440-42-8	20
Inorganic Parameters:		
16. Aluminum, Total		10
17. Antimony, Total		30
18. Arsenic, Total		10
19. Barium, Total		20
20. Beryllium, Total		5
21. Cadmium, Total		5
22. Calcium, Total		40
23. Chromium, Total		10
24. Chromium,Hexavalent	18540-29-9	30
25. Cobalt, Total		10
26. Copper, Total		10
27. Cyanide, Total		10
28. Iron, Total		100
29. Lead, Total		5
30. Magnesium, Total		5
31. Manganese, Total		15
32. Mercury, Total		0.2
33. Nickel, Total		40
34. Potassium, Total		40
35. Selenium, Total		5
36. Silver, Total		10
37. Sodium, Total		10

6 NYCRR Part 360 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

Parameter	CAS Number	Contract Required Quantitation Level (µg/L)
Baseline Parameters (Continued)		
Inorganic Parameters (continued):		
38. Thallium, Total		10
39. Vanadium, Total		40
40. Zinc, Total		20
Organic Parameters:		
1. Acetone	67-64-1	5
2. Acrylonitrile	107-13-1	10
3. Benzene	71-43-2	1
4. Bromochlormethane	74-97-5	1
5. Bromodichloromethane	75-27-4	1
6. Bromoform	75-25-2	1
7. Bromomethane	74-83-9	1
8. 2-Butanone	78-93-3	5
9. Carbon disulfide	75-15-0	1
10. Carbon tetrachloride	56-23-5	1
11. Chlorobenzene	108-90-7	1
12. Chloroethane	75-00-3	1
13. Chloroform	67-66-3	1
14. Chloromethane	74-87-3	1
15. Dibromochloromethane	124-48-1	1
16. 1,2-Dibromo-3-chloro-propane	96-12-8	1
17. 1,2-Dibromoethane	106-93-4	1
18. 1,2-Dichlorobenzene	95-50-1	1
19. 1,3-Dichlorobenzene	541-73-1	1
20. 1,4-Dichlorobenzene	106-46-7	1
21. trans-1,4-Dichloro-2-butene	110-57-6	10
22. 1,1-Dichloroethane	75-34-3	1
23. 1,2-Dichloroethane	107-06-2	1
24. 1,1-Dichloroethene	75-35-4	1
25. cis-1,2-Dichloroethene	156-59-2	1
26. trans-1,2-Dichloroethene	156-60-5	1
27. Dichloromethane (Methylene chloride)	75-09-2	2
28. 1,2-Dichloropropane	78-87-5	1
29. cis-1,3-Dichloro-propene	10061-01-5	1

6 NYCRR Part 360 Parameters
Target Compound List (TCL) and
Contract Required Quantitation Limit
(Continued)

	Parameter	CAS Number	Contract Required Quantitation Level (µg/L)
	Baseline Parameters (Continued)		
Organic Parameters (Continued):			
30.	trans-1,3-Dichloro-propene	10061-02-6	1
31.	Ethylbenzene	100-41-4	1
32.	2-Hexanone	591-78-6	5
33.	Iodomethane	74-88-4	1
34.	4-Methyl-2-pentanone	108-10-1	5
35.	Styrene	100-42-5	1
36.	1,1,1,2-Tetrachloroethane	630-20-6	1
37.	1,1,2,2-Tetrachloroethane	79-34-5	1
38.	Tetrachloroethene	127-18-4	1
39.	Toluene	108-88-3	1
40.	1,1,1-Trichloroethane	71-55-6	1
41.	1,1,2-Trichloroethane	79-00-5	1
42.	Trichloroethene	79-01-6	1
43.	Trichlorofluoromethane	75-69-4	1
44.	1,2,3-Trichloropropane	96-18-4	1
45.	Vinyl acetate	108-05-4	1
46.	Vinyl chloride	75-01-4	1
47.	Xylenes (Total)	1330-20-7	1

METHOD 0010

MODIFIED METHOD 5 SAMPLING TRAIN

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of semivolatile Principal Organic Hazardous Compounds (POHCs) from incineration systems (PHS, 1967). This method also may be used to determine particulate emission rates from stationary sources as per EPA Method 5 (see References at end of this method).

2.0 SUMMARY OF METHOD

2.1 Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. Principal components of the train include a high-efficiency glass- or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin. The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semivolatile organic species. Semivolatile species are defined as compounds with boiling points >100°C.

2.2 Comprehensive chemical analyses of the collected sample are conducted to determine the concentration and identity of the organic materials.

3.0 INTERFERENCES

3.1 Oxides of nitrogen (NO_x) are possible interferents in the determination of certain water-soluble compounds such as dioxane, phenol, and urethane; reaction of these compounds with NO_x in the presence of moisture will reduce their concentration. Other possibilities that could result in positive or negative bias are (1) stability of the compounds in methylene chloride, (2) the formation of water-soluble organic salts on the resin in the presence of moisture, and (3) the solvent extraction efficiency of water-soluble compounds from aqueous media. Use of two or more ions per compound for qualitative and quantitative analysis can overcome interference at one mass. These concerns should be addressed on a compound-by-compound basis before using this method.

4.0 APPARATUS AND MATERIALS

4.1 Sampling train:

4.1.1 A schematic of the sampling train used in this method is shown in Figure 1. This sampling train configuration is adapted from EPA Method 5 procedures, and, as such, the majority of the required equipment

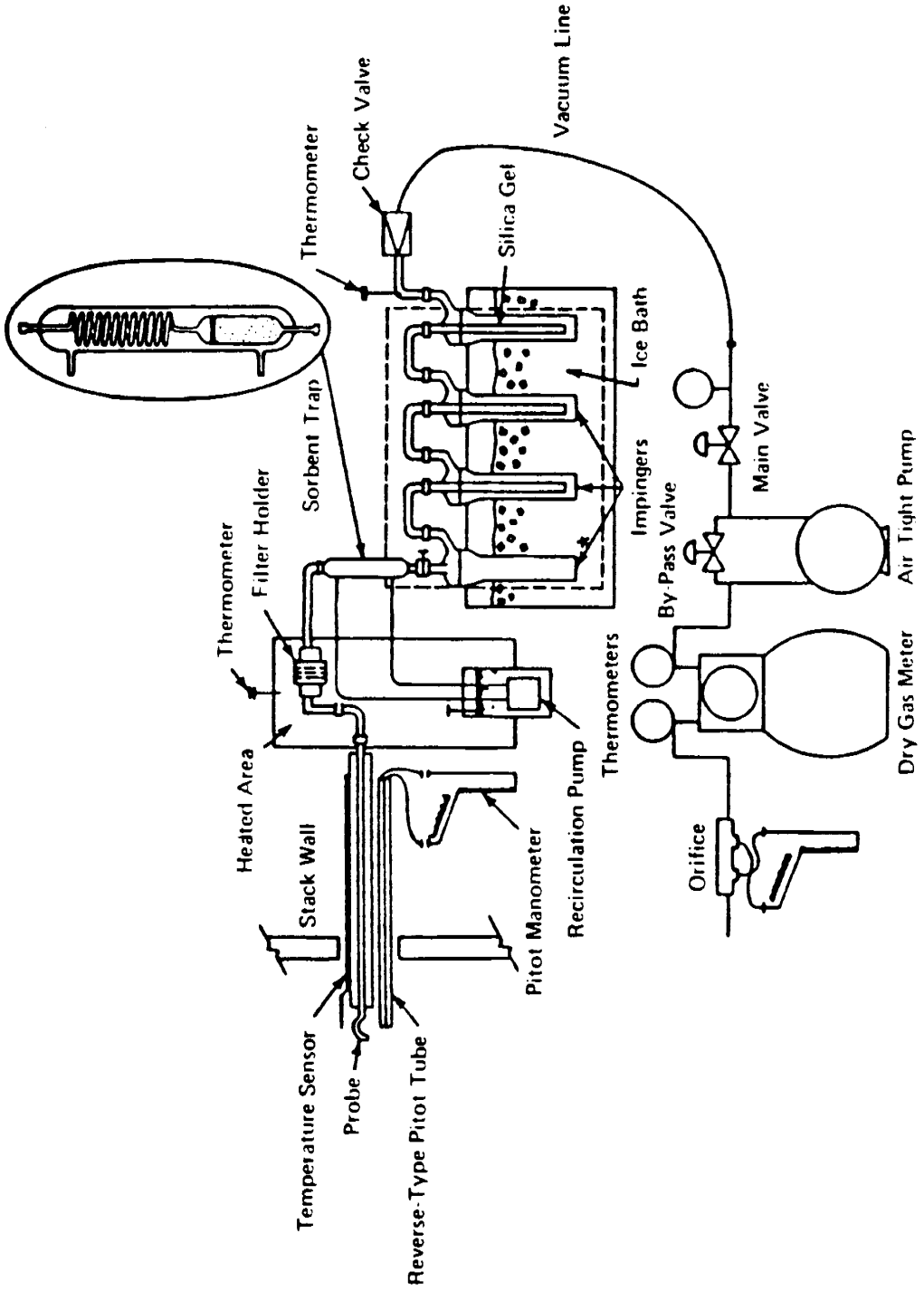


Figure 1. Modified Method 5 Sampling Train.

is identical to that used in EPA Method 5 determinations. The new components required are a condenser coil and a sorbent module, which are used to collect semivolatile organic materials that pass through the glass- or quartz-fiber filter in the gas phase.

4.1.2 Construction details for the basic train components are given in APTD-0581 (see Martin, 1971, in Section 13.0, References); commercial models of this equipment are also available. Specifications for the sorbent module are provided in the following subsections. Additionally, the following subsections list changes to APTD-0581 and identify allowable train configuration modifications.

4.1.3 Basic operating and maintenance procedures for the sampling train are described in APTD-0576 (see Rom, 1972, in Section 13.0, References). As correct usage is important in obtaining valid results, all users should refer to APTD-0576 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

4.1.3.1 Probe nozzle: Stainless steel (316) or glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant I.D. The nozzle shall be buttonhook or elbow design and constructed from seamless tubing (if made of stainless steel). Other construction materials may be considered for particular applications. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32-1.27 cm (1/8-1/2 in.), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Paragraph 9.1.

4.1.3.2 Probe liner: Borosilicate or quartz-glass tubing with a heating system capable of maintaining a gas temperature of 120 $\pm$ 14°C (248 $\pm$ 25°F) at the exit end during sampling. (The tester may opt to operate the equipment at a temperature lower than that specified.) Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) are considered acceptable. Either borosilicate or quartz-glass probe liners may be used for stack temperatures up to about 480°C (900°F). Quartz liners shall be used for temperatures between 480 and 900°C (900 and 1650°F). (The softening temperature for borosilicate is 820°C (1508°F), and for quartz 1500°C (2732°F).) Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500°C.

4.1.3.3 Pitot tube: Type S, as described in Section 2.1 of EPA Method 2, or other appropriate devices (Vollaro, 1976). The pitot tube shall be attached to the probe to allow constant monitoring of the stack-gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2.

4.1.3.4 Differential pressure gauge: Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2. One manometer shall be used for velocity-head (ΔP) readings and the other for orifice differential pressure (ΔH) readings.

4.1.3.5 Filter holder: Borosilicate glass, with a glass frit filter support and a sealing gasket. The sealing gasket should be made of materials that will not introduce organic material into the gas stream at the temperature at which the filter holder will be maintained. The gasket shall be constructed of Teflon or materials of equal or better characteristics. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone or cyclone bypass.

4.1.3.6 Filter heating system: Any heating system capable of maintaining a temperature of 120 $\pm$ 14°C (248 $\pm$ 25°F) around the filter holder during sampling. Other temperatures may be appropriate for particular applications. Alternatively, the tester may opt to operate the equipment at temperatures other than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

4.1.3.7 Organic sampling module: This unit consists of three sections, including a gas-conditioning section, a sorbent trap, and a condensate knockout trap. The gas-conditioning system shall be capable of conditioning the gas leaving the back half of the filter holder to a temperature not exceeding 20°C (68°F). The sorbent trap shall be sized to contain approximately 20 g of porous polymeric resin (Rohm and Haas XAD-2 or equivalent) and shall be jacketed to maintain the internal gas temperature at 17 $\pm$ 3°C (62.5 $\pm$ 5.4°F). The most commonly used coolant is ice water from the impinger ice-water bath, constantly circulated through the outer jacket, using rubber or plastic tubing and a peristaltic pump. The sorbent trap should be outfitted with a glass well or depression, appropriately sized to accommodate a small thermocouple in the trap for monitoring the gas entry temperature. The condensate knockout trap shall be of sufficient size to collect the condensate following gas conditioning. The organic module components shall be oriented to direct the flow of condensate formed vertically downward from the conditioning section, through the adsorbent media, and into the condensate knockout trap. The knockout trap is usually similar in appearance to an empty impinger directly underneath the sorbent module; it may be oversized but should have a shortened center stem (at a minimum, one-half the length of the normal impinger stems) to collect a large volume of condensate without bubbling and overflowing into the impinger train. All surfaces of the organic module wetted by the gas sample shall be fabricated of borosilicate glass, Teflon, or other inert materials. Commercial versions of the

complete organic module are not currently available, but may be assembled from commercially available laboratory glassware and a custom-fabricated sorbent trap. Details of two acceptable designs are shown in Figures 2 and 3 (the thermocouple well is shown in Figure 2).

4.1.3.8 Impinger train: To determine the stack-gas moisture content, four 500-mL impingers, connected in series with leak-free ground-glass joints, follow the knockout trap. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (1/2-in.) I.D. glass tube extending about 1.3 cm (1/2 in.) from the bottom of the outer cylinder. The second impinger shall be of the Greenburg-Smith design with the standard tip. The first and second impingers shall contain known quantities of water or appropriate trapping solution. The third shall be empty or charged with a caustic solution, should the stack gas contain hydrochloric acid (HCl). The fourth shall contain a known weight of silica gel or equivalent desiccant.

4.1.3.9 Metering system: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1%, and related equipment, as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry-gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems capable of maintaining sampling rates within 10% of isokineticity and of determining sample volumes to within 2% may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates. Sampling trains using metering systems designed for flow rates higher than those described in APTD-0581 and APTD-0576 may be used, provided that the specifications of this method are met.

4.1.3.10 Barometer: Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30-m (100 ft) elevation increase (vice versa for elevation decrease).

4.1.3.11 Gas density determination equipment: Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of EPA Method 2), and gas analyzer, if necessary (as described in EPA Method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal.

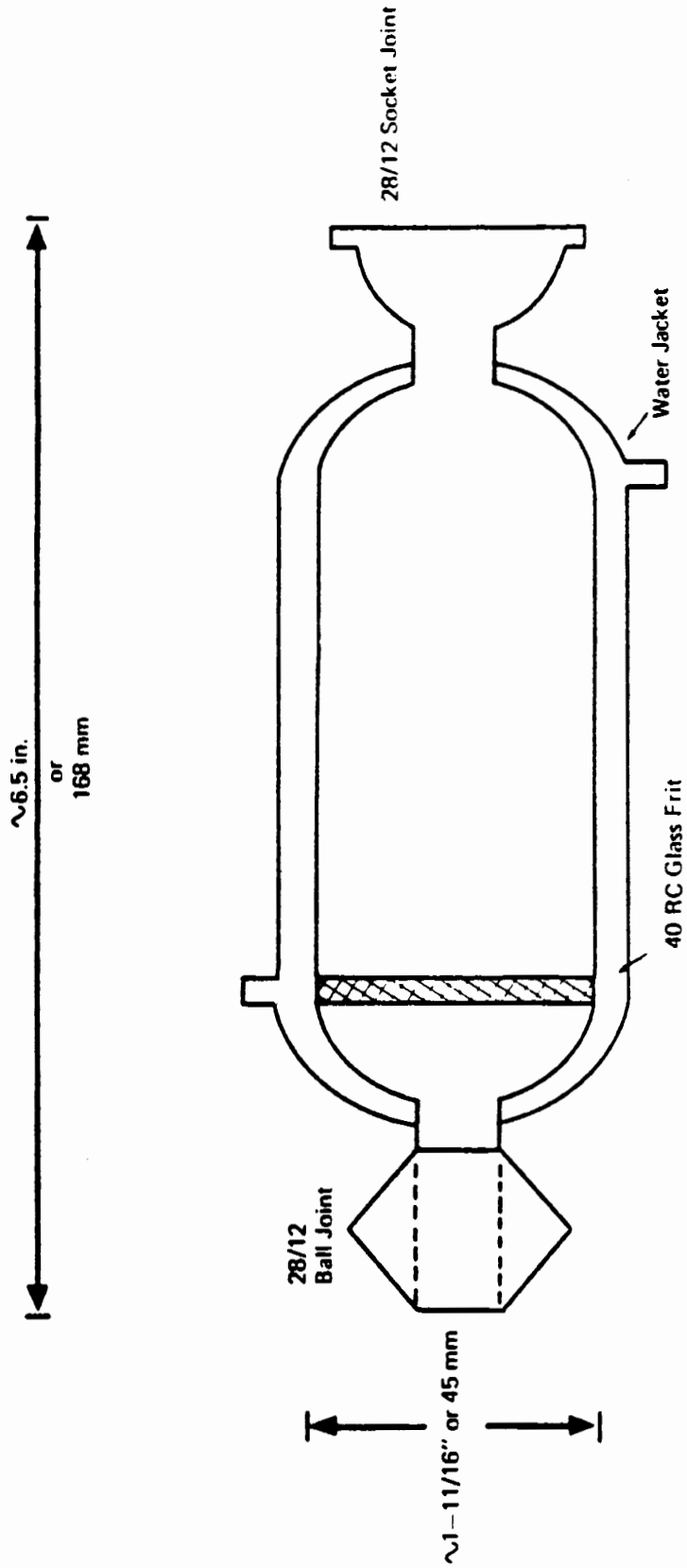


Figure 2. Adsorbent Sampling System.

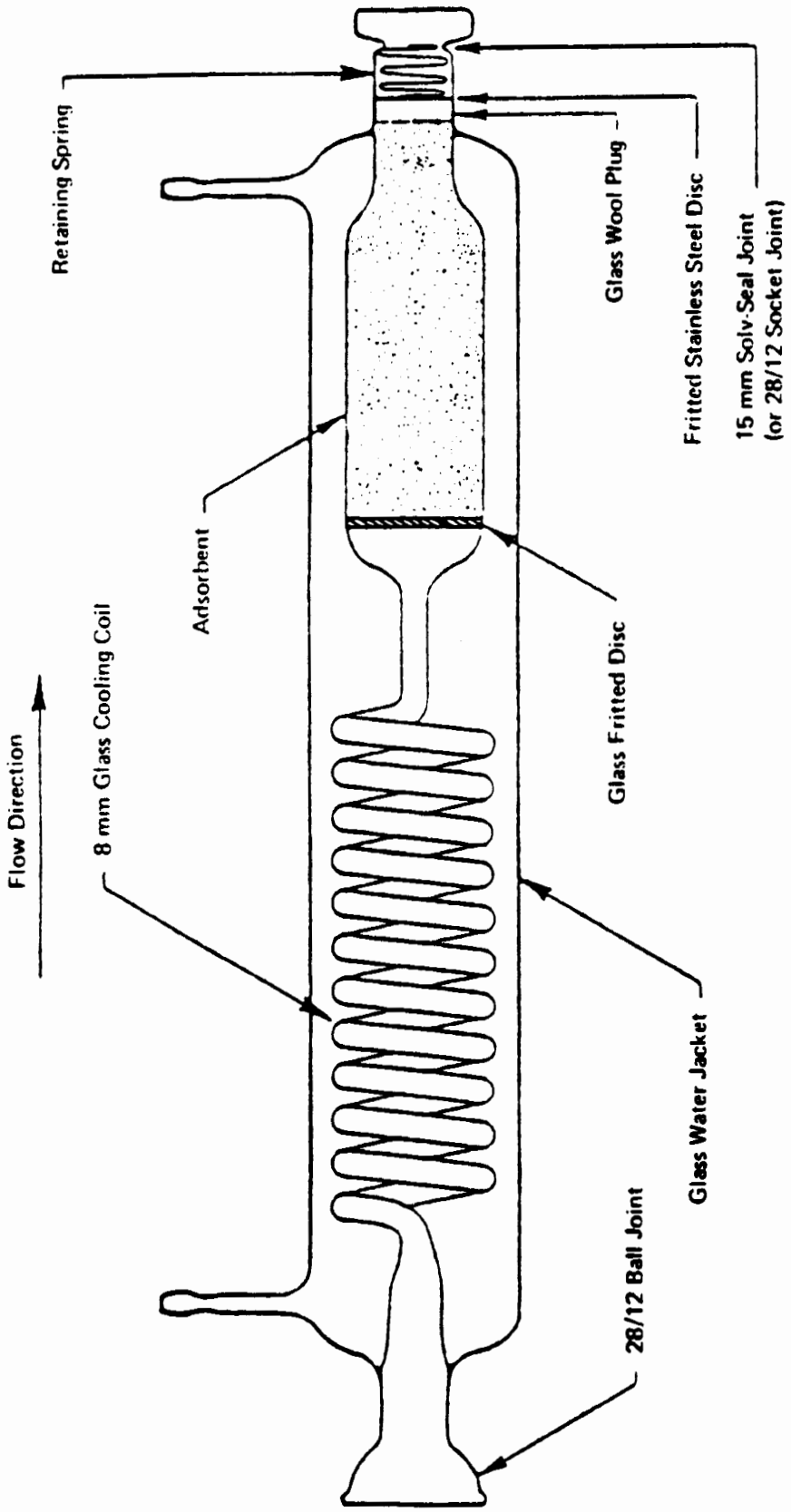


Figure 3. Adsorbent Sampling System.

Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see EPA Method 2, Figure 2-7). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

4.1.3.12 Calibration/field-preparation record: A permanently bound laboratory notebook, in which duplicate copies of data may be made as they are being recorded, is required for documenting and recording calibrations and preparation procedures (i.e., filter and silica gel tare weights, clean XAD-2, quality assurance/quality control check results, dry-gas meter, and thermocouple calibrations, etc.). The duplicate copies should be detachable and should be stored separately in the test program archives.

4.2 Sample Recovery:

4.2.1 **Probe liner:** Probe nozzle and organic module conditioning section brushes; nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the organic module conditioning section.

4.2.2 **Wash bottles:** Three. Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

4.2.3 **Glass sample storage containers:** Chemically resistant, borosilicate amber and clear glass bottles, 500-mL or 1,000-mL. Bottles should be tinted to prevent action of light on sample. Screw-cap liners shall be either Teflon or constructed so as to be leak-free and resistant to chemical attack by organic recovery solvents. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

4.2.4 **Petri dishes:** Glass, sealed around the circumference with wide (1-in.) Teflon tape, for storage and transport of filter samples.

4.2.5 **Graduated cylinder and/or balances:** To measure condensed water to the nearest 1 mL or 1 g. Graduated cylinders shall have subdivisions not >2 mL. Laboratory triple-beam balances capable of weighing to $\pm$0.5 g or better are required.

4.2.6 **Plastic storage containers:** Screw-cap polypropylene or polyethylene containers to store silica gel.

4.2.7 **Funnel and rubber policeman:** To aid in transfer of silica gel to container (not necessary if silica gel is weighed in field).

4.2.8 **Funnels:** Glass, to aid in sample recovery.

4.3 Filters: Glass- or quartz-fiber filters, without organic binder, exhibiting at least 99.95% efficiency (<0.05% penetration) on 0.3-um dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reeve Angel 934 AH or Schleicher and Schwell #3 filters work well under these conditions.

4.4 Crushed ice: Quantities ranging from 10-50 lb may be necessary during a sampling run, depending on ambient air temperature.

4.5 Stopcock grease: Solvent-insoluble, heat-stable silicone grease. Use of silicone grease upstream of the module is not permitted, and amounts used on components located downstream of the organic module shall be minimized. Silicone grease usage is not necessary if screw-on connectors and Teflon sleeves or ground-glass joints are used.

4.6 Glass wool: Used to plug the unfritted end of the sorbent module. The glass-wool fiber should be solvent-extracted with methylene chloride in a Soxhlet extractor for 12 hr and air-dried prior to use.

5.0 REAGENTS

5.1 Adsorbent resin: Porous polymeric resin (XAD-2 or equivalent) is recommended. These resins shall be cleaned prior to their use for sample collection. Appendix A of this method should be consulted to determine appropriate precleaning procedure. For best results, resin used should not exhibit a blank of higher than 4 mg/kg of total chromatographable organics (TCO) (see Appendix B) prior to use. Once cleaned, resin should be stored in an airtight, wide-mouth amber glass container with a Teflon-lined cap or placed in one of the glass sorbent modules tightly sealed with Teflon film and elastic bands. The resin should be used within 4 wk of the preparation.

5.2 Silica gel: Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hr before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

5.3 Impinger solutions: Distilled organic-free water (Type II) shall be used, unless sampling is intended to quantify a particular inorganic gaseous species. If sampling is intended to quantify the concentration of additional species, the impinger solution of choice shall be subject to Administrator approval. This water should be prescreened for any compounds of interest. One hundred mL will be added to the specified impinger; the third impinger in the train may be charged with a basic solution (1 N sodium hydroxide or sodium acetate) to protect the sampling pump from acidic gases. Sodium acetate should be used when large sample volumes are anticipated because sodium hydroxide will react with carbon dioxide in aqueous media to form sodium carbonate, which may possibly plug the impinger.

5.4 Sample recovery reagents:

5.4.1 **Methylene chloride:** Distilled-in-glass grade is required for sample recovery and cleanup (see Note to 5.4.2 below).

5.4.2 **Methyl alcohol:** Distilled-in-glass grade is required for sample recovery and cleanup.

NOTE: Organic solvents from metal containers may have a high residue blank and should not be used. Sometimes suppliers transfer solvents from metal to glass bottles; thus blanks shall be run prior to field use and only solvents with low blank value (<0.001%) shall be used.

5.4.3 **Water:** Water (Type II) shall be used for rinsing the organic module and condenser component.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Because of complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

6.2 Laboratory preparation:

6.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified.

6.2.2 Weigh several 200- to 300-g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

6.2.3 Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass Petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

6.2.4 Desiccate the filters at 20 ± 5.6°C (68 ± 10°F) and ambient pressure for at least 24 hr, and weigh at intervals of at least 6 hr to a constant weight (i.e., <0.5-mg change from previous weighing), recording results to the nearest 0.1 mg. During each weighing the filter must not be exposed for more than a 2-min period to the laboratory atmosphere and relative humidity above 50%. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 105°C (220°F) for 2-3 hr, desiccated for 2 hr, and weighed.

6.3 Preliminary field determinations:

6.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. It is recommended that a leak-check of the pitot lines (see EPA Method 2, Section 3.1) be performed. Determine the stack-gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack-gas dry molecular weight, as described in EPA Method 2, Section 3.6. If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

6.3.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2).

6.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

6.3.4 A minimum of 3 dscm (105.9 dscf) of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of POHCs from incineration systems. Additional sample volume shall be collected as necessitated by analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in Section 10.0.

6.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min.

6.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-sample volumes. In these cases, the Administrator's approval must first be obtained.

6.4 Preparation of collection train:

6.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon film or aluminum foil until just prior to assembly or until sampling is about to begin.

6.4.2 Fill the sorbent trap section of the organic module with approximately 20 g of clean adsorbent resin. While filling, ensure that the trap packs uniformly, to eliminate the possibility of channeling. When freshly cleaned, many adsorbent resins carry a static charge, which will cause clinging to trap walls. This may be minimized by filling the trap in the presence of an antistatic device. Commercial antistatic devices include Model-204 and Model-210 manufactured by the 3M Company, St. Paul, Minnesota.

6.4.3 If an impinger train is used to collect moisture, place 100 mL of water in each of the first two impingers, leave the third impinger empty (or charge with caustic solution, as necessary), and transfer approximately 200-300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

6.4.4 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

6.4.5 When glass liners are used, install the selected nozzle using a Viton-A O-ring when stack temperatures are <260°C (500°F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connecting systems utilizing either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above, or by a leak-free direct mechanical connection. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

6.4.6 Set up the train as in Figure 1. During assembly, do not use any silicone grease on ground-glass joints that are located upstream of the organic module. A very light coating of silicone grease may be used on all ground-glass joints that are located downstream of the organic module, but it should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone-grease contamination. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack. The organic module condenser must be maintained at a temperature of 17 $\pm$ 3°C. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

6.4.7 Place crushed ice around the impingers and the organic module condensate knockout.

6.4.8 Turn on the sorbent module and condenser coil coolant recirculating pump and begin monitoring the sorbent module gas entry temperature. Ensure proper sorbent module gas entry temperature before proceeding and again before any sampling is initiated. It is extremely important that the XAD-2 resin temperature never exceed 50°C (122°F), because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20°C (68°F) for efficient capture of the semivolatile species of interest.

6.4.9 Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

6.5 Leak-check procedures

6.5.1 **Pre-test leak-check:**

6.5.1.1 Because the number of additional intercomponent connections in the Semi-VOST train (over the M5 Train) increases the possibility of leakage, a pre-test leak-check is required.

6.5.1.2 After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381-mm Hg (15-in. Hg) vacuum.
(NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.)

6.5.1.3 If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first attaching a carbon-filled leak-check impinger (shown in Figure 4) to the inlet of the filter holder (cyclone, if applicable) and then plugging the inlet and pulling a 381-mm Hg (15-in. Hg) vacuum. (Again, a lower vacuum may be used, provided that it is not exceeded during the test.) Then, connect the probe to the train and leak-check at about 25-mm Hg (1-in. Hg) vacuum; alternatively, leak-check the probe with the rest of the sampling train in one step at 381-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4% of the average sampling rate or >0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

6.5.1.4 The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with fine-adjust valve fully open and coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve; this will cause water to back up into the organic module. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

CROSS SECTIONAL VIEW

Leak Testing Apparatus

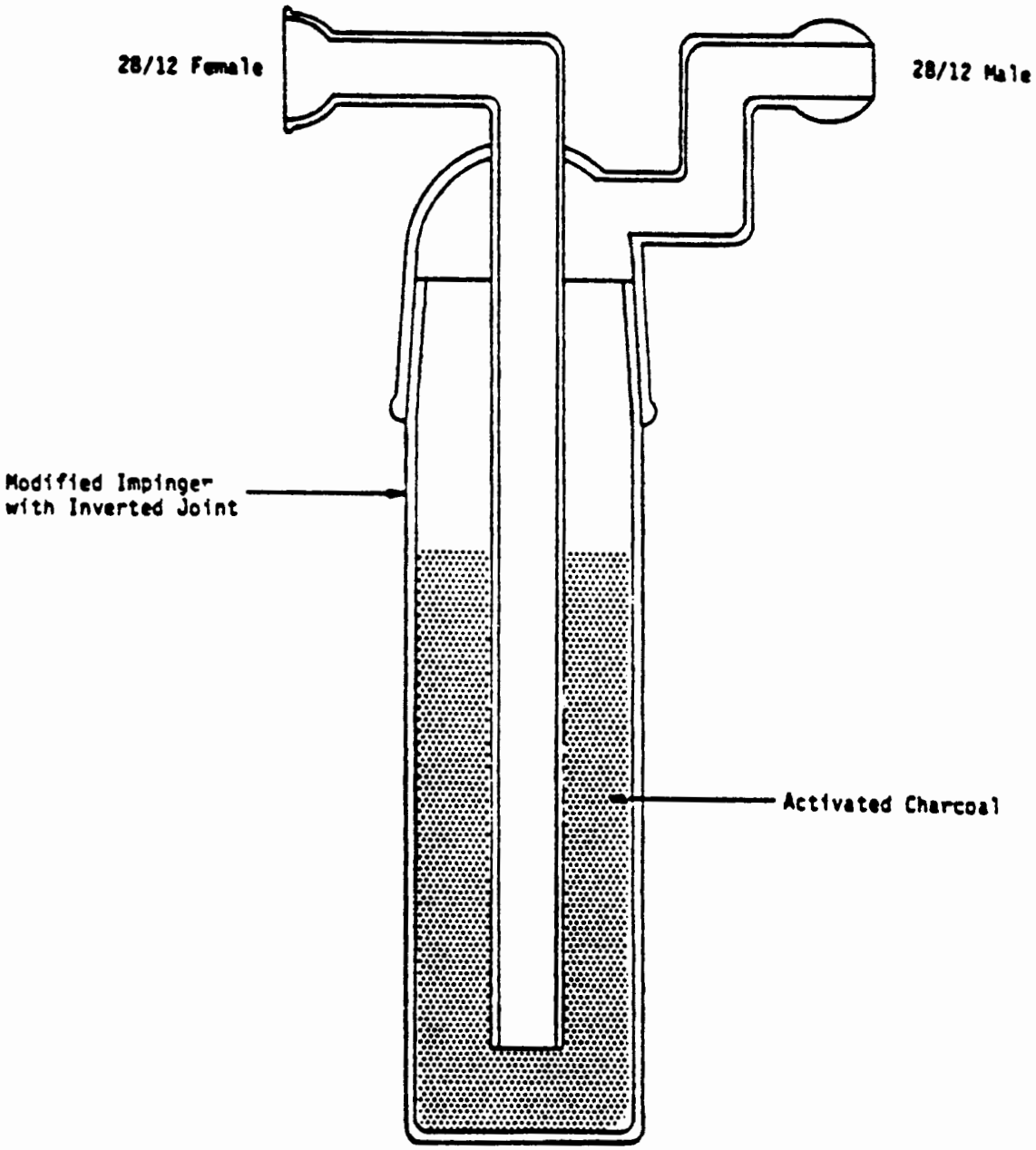


Figure 4. Leak-check Impinger

6.5.1.5 When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable). When the vacuum drops to 127 mm (5 in.) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed. This prevents the water in the impingers from being forced backward into the organic module and silica gel from being entrained backward into the third impinger.

6.5.2 **Leak-checks during sampling run:**

6.5.2.1 If, during the sampling run, a component (e.g., filter assembly, impinger, or sorbent trap) change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Paragraph 6.5.1, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If a higher leakage rate is obtained, the tester shall void the sampling run. (It should be noted that any "correction" of the sample volume by calculation by calculation reduces the integrity of the pollutant concentrations data generated and must be avoided.)

6.5.2.2 Immediately after a component change, and before sampling is reinitiated, a leak-check similar to a pre-test leak-check must also be conducted.

6.5.3 **Post-test leak-check:**

6.5.3.1 A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done with the same procedures as those with the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate, correct the sample volume (as shown in the calculation section of this method), and consider the data obtained of questionable reliability, or void the sampling run.

6.6 Sampling-train operation:

6.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, unless otherwise specified by the Administrator. Maintain a temperature around the filter of 120 ± 14°C (248 ± 25°F) and a gas temperature entering the sorbent trap at a maximum of 20°C (68°F).

6.6.2 For each run, record the data required on a data sheet such as the one shown in Figure 5. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings required by Figure 5 at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity-head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

6.6.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot-tube coefficient is 0.84 $\pm$ 0.02 and the stack-gas equivalent density (dry molecular weight) is equal to 29 $\pm$ 4. APTD-0576 details the procedure for using the nomographs. If the stack-gas molecular weight and the pitot-tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps (Shigehara, 1974) are taken to compensate for the deviations.

6.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack, to prevent water from backing into the organic module. If necessary, the pump may be turned on with the coarse-adjust valve closed.

6.6.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

6.6.6 Traverse the stack cross section, as required by EPA Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

6.6.7 During the test run, make periodic adjustments to keep the temperature around the filter holder and the organic module at the proper levels; add more ice and, if necessary, salt to maintain a temperature of <20°C (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

Plant _____
Location _____
Operator _____
Date _____
Run No. _____
Sample Box No. _____
Meter Box No. _____
Meter ΔH _____
C Factor _____
Pitot Tube Coefficient C_p _____

Schematic of Stack Cross Section

Ambient Temperature _____
Barometric Pressure _____
Assumed Moisture % _____
Probe Length, m (ft) _____
Nozzle Identification No. _____
Average Calibrated Nozzle Diameter, cm (in) _____
Probe Heater Setting _____
Leak Rate, m^3/min, (cfm) _____
Probe Liner Material _____
Static Pressure, mm Hg (in. Hg) _____
Filter No. _____

Traverse Point Number	Sampling Time (θ) min.	Vacuum mm Hg (in. Hg)	Stack Temperature (T_s) °C(°F)	Velocity Head ($\sqrt{P_s}$) mm (in) H_2O	Pressure Differential Across Orifice Meter mm (H_2O) (in H_2O)	Gas Sample Volume m_3 (ft_3)	Gas Sample Temp. at Dry Gas Meter Inlet °C(°F)	Gas Sample Temp. at Dry Gas Meter Outlet °C(°F)	Filter Holder Temperature °C(F°)	Temperature of Gas Entering Sorbet Trap °C(F°)	Temperature of Gas Leaving Condenser or Last Impinger
Total							Avg.	Avg.			
Average											

Figure 5. Particulate field data.

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6.6.8 If the pressure drop across the filter or sorbent trap becomes too high, making isokinetic sampling difficult to maintain, the filter/sorbent trap may be replaced in the midst of a sample run. Using another complete filter holder/sorbent trap assembly is recommended, rather than attempting to change the filter and resin themselves. After a new filter/sorbent trap assembly is installed, conduct a leak-check. The total particulate weight shall include the summation of all filter assembly catches.

6.6.9 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

6.6.10 Note that when two or more trains are used, separate analysis of the front-half (if applicable) organic-module and impinger (if applicable) catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In that case, the front-half catches from the individual trains may be combined (as may the impinger catches), and one analysis of front-half catch and one analysis of impinger catch may be performed.

6.6.11 At the end of the sample run, turn off the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry-gas meter reading, and conduct a post-test leak-check. Also, leak-check the pitot lines as described in EPA Method 2. The lines must pass this leak-check in order to validate the velocity-head data.

6.6.12 Calculate percent isokineticity (see Section 10.8) to determine whether the run was valid or another test run should be made.

7.0 SAMPLE RECOVERY

7.1 Preparation:

7.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the sorbent module.

7.1.2 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet, being careful not to lose any condensate that might be present. Cap the filter inlet.

Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the organic module and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the organic module.

7.1.3 Cap the filter-holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas-conditioning section. Cap all organic module openings. Disconnect the organic-module knockout trap from the impinger train inlet and cap both of these openings. Ground-glass stoppers, Teflon caps, or caps of other inert materials may be used to seal all openings.

7.1.4 Transfer the probe, the filter, the organic-module components, and the impinger/condenser assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

7.1.5 Save a portion of all washing solutions (methanol/methylene chloride, Type II water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle being used and place each in a separate, prelabeled glass sample container.

7.1.6 Inspect the train prior to and during disassembly and note any abnormal conditions.

7.2 Sample containers:

7.2.1 **Container no. 1:** Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use a pair or pairs of tweezers to handle the filter. If it is necessary to fold the filter, ensure that the particulate cake is inside the fold. Carefully transfer to the Petri dish any particulate matter or filter fibers that adhere to the filter-holder gasket, using a dry nylon bristle brush or sharp-edged blade, or both. Label the container and seal with 1-in.-wide Teflon tape around the circumference of the lid.

7.2.2 **Container no. 2:** Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components first with methanol/methylene chloride (1:1 v/v) into a glass container. Distilled water may also be used. Retain a water and solvent blank and analyze in the same manner as with the samples. Perform rinses as follows:

7.2.2.1 Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent mixture (1:1 v/v methanol/-methylene chloride) from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particles; then make a final rinse of the inside surface with the solvent mix. Brush and rinse the inside parts of the Swagelok fitting with the solvent mix in a similar way until no visible particles remain.

7.2.2.2 Have two people rinse the probe liner with the solvent mix by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washes to the container.

7.2.2.3 Follow the solvent rinse with a probe brush. Hold the probe in an inclined position and squirt solvent into the upper end while pushing the probe brush through the probe with a twisting action; place a sample container underneath the lower end of the probe and catch any solvent and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the solvent or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above-prescribed manner at least six times (metal probes have small crevices in which particulate matter can be entrapped). Rinse the brush with solvent and quantitatively collect these washings in the sample container. After the brushing, make a final solvent rinse of the probe as described above.

7.2.2.4 It is recommended that two people work together to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

7.2.2.5 Clean the inside of the front half of the filter holder and cyclone/cyclone flask, if used, by rubbing the surfaces with a nylon bristle brush and rinsing with methanol/methylene chloride (1:1 v/v) mixture. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if applicable). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all solvent washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that solvent will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents.

7.2.3 **Container no. 3:** The sorbent trap section of the organic module may be used as a sample transport container, or the spent resin may be transferred to a separate glass bottle for shipment. If the sorbent trap itself is used as the transport container, both ends should be sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon caps may be used. The sorbent trap should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If a separate bottle is used, the spent resin should be quantitatively transferred from the trap into the clean bottle. Resin that adheres to the walls of the trap should be recovered using a rubber policeman or spatula and added to this bottle.

7.2.4 **Container no. 4:** Measure the volume of condensate collected in the condensate knockout section of the organic module to within ±1 mL by using a graduated cylinder or by weighing to within ±0.5 g using a triple-beam balance. Record the volume or weight of liquid present and note any discoloration or film in the liquid catch. Transfer this liquid to a prelabeled glass sample container. Inspect the back half of the filter housing and the gas-conditioning section of the organic module. If condensate is observed, transfer it to a graduated or weighing bottle and measure the volume, as described above. Add this material to the condensate knockout-trap catch.

7.2.5 **Container no. 5:** All sampling train components located between the high-efficiency glass- or quartz-fiber filter and the first wet impinger or the final condenser system (including the heated Teflon line connecting the filter outlet to the condenser) should be thoroughly rinsed with methanol/methylene chloride (1:1 v/v) and the rinsings combined. This rinse shall be separated from the condensate. If the spent resin is transferred from the sorbent trap to a separate sample container for transport, the sorbent trap shall be thoroughly rinsed until all sample-wetted surfaces appear clean. Visible films should be removed by brushing. Whenever train components are brushed, the brush should be subsequently rinsed with solvent mixture and the rinsings added to this container.

7.2.6 **Container no. 6:** Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere strongly to the impinger wall. Because the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

7.3 Impinger water:

7.3.1 Make a notation of any color or film in the liquid catch. Measure the liquid in the first three impingers to within ±1 mL by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

7.3.2 Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see Paragraph 4.1.3.7). Amber glass containers should be used for storage of impinger catch, if required.

7.3.3 If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

7.4 Sample preparation for shipment: Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward. The particulate filters should be shipped unrefrigerated.

8.0 ANALYSIS

8.1 Sample preparation:

8.1.1 **General:** The preparation steps for all samples will result in a finite volume of concentrated solvent. The final sample volume (usually in the 1- to 10-mL range) is then subjected to analysis by GC/MS. All samples should be inspected and the appearance documented. All samples are to be spiked with surrogate standards as received from the field prior to any sample manipulations. The spike should be at a level equivalent to 10 times the MDL when the solvent is reduced in volume to the desired level (i.e., 10 mL). The spiking compounds should be the stable isotopically labeled analog of the compounds of interest or a compound that would exhibit properties similar to the compounds of interest, be easily chromatographed, and not interfere with the analysis of the compounds of interest. Suggested surrogate spiking compounds are: deuterated naphthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and carbon-13-labeled pentachlorophenol.

8.1.2 **Condensate:** The "condensate" is the moisture collected in the first impinger following the XAD-2 module. Spike the condensate with the surrogate standards. The volume is measured and recorded and then transferred to a separatory funnel. The pH is to be adjusted to pH 2 with 6 N sulfuric acid, if necessary. The sample container and graduated cylinder are sequentially rinsed with three successive 10-mL aliquots of the extraction solvent and added to the separatory funnel. The ratio of solvent to aqueous sample should be maintained at 1:3. Extract the sample by vigorously shaking the separatory funnel for 5 min. After complete separation of the phases, remove the solvent and transfer to a Kuderna-Danish concentrator (K-D), filtering through a bed of precleaned, dry sodium sulfate. Repeat the extraction step two additional times. Adjust the pH to 11 with 6 N sodium hydroxide and reextract combining the acid and base extracts. Rinse the sodium sulfate into the K-D with fresh solvent and discard the desiccant. Add Teflon boiling chips and concentrate to 10 mL by reducing the volume to slightly less than 10 mL and then bringing to volume with fresh solvent. In order to achieve the necessary detection limit, the sample volume can be further reduced to 1 mL by using a micro column K-D or nitrogen blow-down. Should the sample start to exhibit precipitation, the concentration step should be stopped and the sample redissolved with fresh solvent taking the volume to some finite amount. After adding a standard (for the purpose of quantitation by GC/MS), the sample is ready for analysis, as discussed in Paragraph 8.2.

8.1.3 **Impinger:** Spike the sample with the surrogate standards; measure and record the volume and transfer to a separatory funnel. Proceed as described in Paragraph 8.1.2.

8.1.4 **XAD-2:** Spike the resin directly with the surrogate standards. Transfer the resin to the all-glass thimbles by the following procedure (care should be taken so as not to contaminate the thimble by touching it with anything other than tweezers or other solvent-rinsed mechanical holding devices). Suspend the XAD-2 module directly over the thimble. The glass frit of the module (see Figure 2) should be in the up position. The thimble is contained in a clean beaker, which will serve to catch the solvent rinses. Using a Teflon squeeze bottle, flush the XAD-2 into the thimble. Thoroughly rinse the glass module with solvent into the beaker containing the thimble. Add the XAD-2 glass-wool plug to the thimble. Cover the XAD-2 in the thimble with a precleaned glass-wool plug sufficient to prevent the resin from floating into the solvent reservoir of the extractor. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. If a question arises concerning the completeness of the extraction, a second extraction, without a spike, is advised. The thimble is placed in the extractor and the rinse solvent contained in the beaker is added to the solvent reservoir. Additional solvent is added to make the reservoir approximately two-thirds full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle 5-6 times per hr. Extract the resin for 16 hr. Transfer the solvent and three 10-mL rinses of the reservoir to a K-D and concentrate as described in Paragraph 8.1.2.

8.1.5 **Particulate filter (and cyclone catch):** If particulate loading is to be determined, weigh the filter (and cyclone catch, if applicable). The particulate filter (and cyclone catch, if applicable) is transferred to the glass thimble and extracted simultaneously with the XAD-2 resin.

8.1.6 **Train solvent rinses:** All train rinses (i.e., probe, impinger, filter housing) using the extraction solvent and methanol are returned to the laboratory as a single sample. If the rinses are contained in more than one container, the intended spike is divided equally among the containers proportioned from a single syringe volume. Transfer the rinse to a separatory funnel and add a sufficient amount of organic-free water so that the methylene chloride becomes immiscible and its volume no longer increases with the addition of more water. The extraction and concentration steps are then performed as described in Paragraph 8.1.2.

8.2 Sample analysis:

8.2.1 The primary analytical tool for the measurement of emissions from hazardous waste incinerators is GC/MS using fused-silica capillary GC columns, as described in Method 8270 in Chapter Four of this manual. Because of the nature of GC/MS instrumentation and the cost associated

with sample analysis, prescreening of the sample extracts by gas chromatography/flame ionization detection (GC/FID) or with electron capture (GC/ECD) is encouraged. Information regarding the complexity and concentration level of a sample prior to GC/MS analysis can be of enormous help. This information can be obtained by using either capillary columns or less expensive packed columns. However, the FID screen should be performed with a column similar to that used with the GC/MS. Keep in mind that GC/FID has a slightly lower detection limit than GC/MS and, therefore, that the concentration of the sample can be adjusted either up or down prior to analysis by GC/MS.

8.2.2 The mass spectrometer will be operated in a full scan (40-450) mode for most of the analyses. The range for which data are acquired in a GC/MS run will be sufficiently broad to encompass the major ions, as listed in Chapter Four, Method 8270, for each of the designated POHCs in an incinerator effluent analysis.

8.2.3 For most purposes, electron ionization (EI) spectra will be collected because a majority of the POHCs give reasonable EI spectra. Also, EI spectra are compatible with the NBS Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

8.2.4 To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions will be used to elucidate molecular-weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification. Refer to Chapter Four, Method 8270, for complete descriptions of GC conditions, MS conditions, and quantitative and quantitative identification.

9.0 CALIBRATION

9.1 Probe nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

9.2 Pitot tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked, dented, or corroded and if it meets design and intercomponent spacing specifications.

9.3 Metering system:

9.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: Make a 10-min calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

9.3.2 After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

9.3.3 **Leak-check of metering system:** That portion of the sampling train from the pump to the orifice meter (see Figure 1) should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 6): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13-18 cm (5-7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected.

NOTE: If the dry-gas-meter coefficient values obtained before and after a test series differ by >5%, either the test series shall be voided or calculations for test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

9.4 Probe heater: The probe-heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

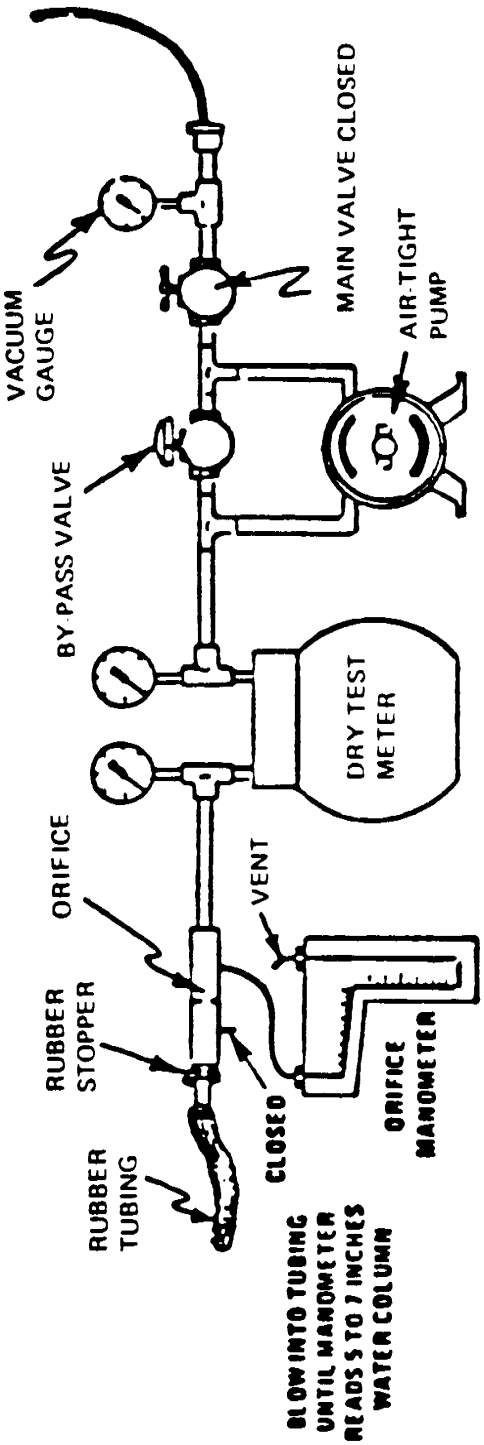

Figure 6. Leak-check of meter box.

9.5 Temperature gauges: Each thermocouple must be permanently and uniquely marked on the casting; all mercury-in-glass reference thermometers must conform to ASTM E-1 63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change >1.5%.

9.5.1 **Impinger, organic module, and dry-gas meter thermocouples:** For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2 resin bed, three-point calibration at ice-water, room-air, and boiling-water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ±2°C (3.6°F) with those of the absolute value of the reference thermometer.

9.5.2 **Probe and stack thermocouple:** For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and hot-oil-bath temperatures must be performed; it is recommended that room-air temperature be added, and that the thermometer and the thermocouple agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

9.6 Barometer: Adjust the barometer initially and before each test series to agree to within ±25 mm Hg (0.1 in. Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

9.7 Triple-beam balance: Calibrate the triple-beam balance before each test series, using Class-S standard weights; the weights must be within ±0.5% of the standards, or the balance must be adjusted to meet these limits.

10.0 CALCULATIONS

10.1 Carry out calculations. Round off figures after the final calculation to the correct number of significant figures.

10.2 Nomenclature:

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for a leak-check, either pre-test or following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak-check conducted prior to the "i^{th}" component change (i = 1, 2, 3...n) m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).

M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack-gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry-gas meter temperature (see Figure 6), K (°R).

T_s = Absolute average stack-gas temperature (see Figure 6), K (°R).

T_{std} = Standard absolute temperature, 293K (528°R).

V_{lc} = Total volume of liquid collected in the organic module condensate knockout trap, the impingers, and silica gel, mL.

V_m = Volume of gas sample as measured by dry-gas meter, dscm (dscf).

$V_{m(std)}$ = Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack-gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

γ = Dry-gas-meter calibration factor, dimensionless.

ΔH = Average pressure differential across the orifice meter (see Figure 2), mm H_2O (in. H_2O).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

θ_1 = Sampling time interval from the beginning of a run until the first component change, min.

θ_i = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent.

10.3 Average dry-gas-meter temperature and average orifice pressure drop: See data sheet (Figure 5, above).

10.4 Dry-gas volume: Correct the sample measured by the dry-gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]) by using Equation 1:

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar} + \Delta H/13.6}{P_{std}} = K_1 V_m Y \frac{P_{bar} + \Delta H/13.6}{T_m} \qquad (1)$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or
K_1 = 17.64°R/in. Hg for English units.

It should be noted that Equation 1 can be used as written, unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 1 must be modified as follows:

a. Case I (no component changes made during sampling run): Replace V_m in Equation 1 with the expression:

$$V_m - (L_p - L_a)$$

b. Case II (one or more component changes made during the sampling run): Replace V_m in Equation 1 by the expression:

$$V_m - (L_1 - L_a)\theta_1 - \sum_{i=2}^{n} (L_i - L_a)\theta_1 - (L_p - L_a)\theta_p$$

and substitute only for those leakage rates (L_1 or L_p) that exceed L_a.

10.5 Volume of water vapor:

$$V_{w(std)} = V_{lc} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{lc} \quad (2)$$

where:

K_2 = 0.001333 m^3/mL for metric units, or
K_2 = 0.04707 ft^3/mL for English units.

10.6 Moisture content:

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad (3)$$

NOTE: In saturated or water-droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 3) and a second from the assumption of saturated conditions. The lower of the two values of B_w shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note to Section 1.2 of Method 4. For the purposes of this method, the average stack-gas temperature from Figure 6 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1°C (2°F).

10.7 Conversion factors:

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

10.8 Isokinetic variation:

10.8.1 **Calculation from raw data:**

$$I = \frac{100\ T_s[K_3 F_{lc} + (V_m/T_m)\ (P_{bar} + \Delta H/13.6)]}{60\theta V_s P_s A_n} \qquad (4)$$

where:

K_3 = 0.003454 mm Hg-m^3/mL-K for metric units, or
K_3 = 0.002669 in. Hg-ft^3/mL-°R for English units.

10.8.2 **Calculation for intermediate values:**

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} V_s \theta A_n P_s 60(1-B_{ws})} \qquad (5)$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta (1-B_{ws})}$$

where:

K_4 = 4.320 for metric units, or
K_4 = 0.09450 for English units.

10.8.3 **Acceptable results:** If 90% $\leq$ I $\leq$ 110%, the results are acceptable. If the results are low in comparison with the standard and I is beyond the acceptable range, or if I is less than 90%, the Administrator may opt to accept the results.

10.9 To determine the minimum sample volume that shall be collected, the following sequence of calculations shall be used.

10.9.1 From prior analysis of the waste feed, the concentration of POHCs introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the maximum amount of POHC allowed to be present in the effluent. This may be expressed as:

$$\frac{(WF)\ (POHC_i\ conc)}{100} \ \frac{(100\text{-}\%DRE)}{100} = \text{Max } POHC_i \text{ Mass} \qquad (6)$$

where:

WF = mass flow rate of waste feed per hr, g/hr (lb/hr).

$POHC_i$ = concentration of Principal Organic Hazardous Compound (wt %) introduced into the combustion process.

DRE = percent Destruction and Removal Efficiency required.

Max POHC = mass flow rate (g/hr [lb/hr]) of POHC emitted from the combustion source.

10.9.2 The average discharge concentration of the POHC in the effluent gas is determined by comparing the Max POHC with the volumetric flow rate being exhausted from the source. Volumetric flow rate data are available as a result of preliminary Method 1-4 determinations:

$$\frac{\text{Max POHC}_i \text{ Mass}}{DV_{eff(std)}} = \text{Max POHC}_i \text{ conc} \qquad (7)$$

where:

$DV_{eff(std)}$ = volumetric flow rate of exhaust gas, dscm (dscf).

$POHC_i$ conc = anticipated concentration of the POHC in the exhaust gas stream, g/dscm (lb/dscf).

10.9.3 In making this calculation, it is recommended that a safety margin of at least ten be included:

$$\frac{LDL_{POHC} \times 10}{POHC_i \text{ conc}} = V_{TBC} \qquad (8)$$

where:

LDL_{POHC} = detectable amount of POHC in entire sampling train.

NOTE: The whole extract from an XAD-2 cartridge is seldom if ever, injected at once. Therefore, if aliquoting factors are involved, the LDL_{POHC} is not the same as the analytical (or column) detection limit.

V_{TBC} = minimum dry standard volume to be collected at dry-gas meter.

10.10 Concentration of any given POHC in the gaseous emissions of a combustion process:

1) Multiply the concentration of the POHC as determined in Method 8270 by the final concentration volume, typically 10 mL.

C_{POHC} (ug/mL) x sample volume (mL) = amount (ug) of POHC in sample (9)

where:

C_{POHC} = concentration of POHC as analyzed by Method 8270.

2) Sum the amount of POHC found in all samples associated with a single train.

Total (ug) = XAD-2 (ug) + condensate (ug) + rinses (ug) + impinger (ug) (10)

3) Divide the total ug found by the volume of stack gas sampled (m^3).

(Total ug)/(train sample volume) = concentration of POHC (ug/m^3) (11)

11.0 QUALITY CONTROL

11.1 Sampling: See EPA Manual 600/4-77-027b for Method 5 quality control.

11.2 Analysis: The quality assurance program required for this study includes the analysis of field and method blanks, procedure validations, incorporation of stable labeled surrogate compounds, quantitation versus stable labeled internal standards, capillary column performance checks, and external performance tests. The surrogate spiking compounds selected for a particular analysis are used as primary indicators of the quality of the analytical data for a wide range of compounds and a variety of sample matrices. The assessment of combustion data, positive identification, and quantitation of the selected compounds are dependent on the integrity of the samples received and the precision and accuracy of the analytical methods employed. The quality assurance procedures for this method are designed to monitor the performance of the analytical method and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

11.2.1 **Field Blanks:** Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, unused filters, and resin cartridges. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train.

11.2.2 **Method blanks:** A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

11.2.3 Refer to Method 8270 for additional quality control considerations.

12.0 METHOD PERFORMANCE

12.1 Method performance evaluation: Evaluation of analytical procedures for a selected series of compounds must include the sample-preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

12.2 Method detection limit: The overall method detection limits (lower and upper) must be determined on a compound-by-compound basis because different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrumental minimum detection limit (MDL). The method detection limit must be quoted relative to a given sample volume. The upper limits for the method must be determined relative to compound retention volumes (breakthrough).

12.3 Method precision and bias: The overall method precision and bias must be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and extraction efficiency of the train components. From evaluation studies to date using a dynamic spiking system, method biases of -13% and -16% have been determined for toluene and 1,1,2,2-tetrachloroethane, respectively. A precision of 19.9% was calculated from a field test data set representing seven degrees of freedom which resulted from a series of paired, unspiked Semivolatile Organic Sampling trains (Semi-VOST) sampling emissions from a hazardous waste incinerator.

13.0 REFERENCES

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PREPARATION OF XAD-2 SORBENT RESIN

1.0 SCOPE AND APPLICATION

1.1 XAD-2 resin as supplied by the manufacturer is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Both the salt solution and any residual extractable monomer and polymer species must be removed before use. The resin is prepared by a series of water and organic extractions, followed by careful drying.

2.0 EXTRACTION

2.1 Method 1: The procedure may be carried out in a giant Soxhlet extractor. An all-glass thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass-wool plug and stainless steel screen because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with Type II water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with H_2O for 8 hr.
Methyl alcohol	Extract for 22 hr.
Methylene chloride	Extract for 22 hr.
Methylene chloride (fresh)	Extract for 22 hr.

2.2 Method 2:

2.2.1 As an alternative to Soxhlet extraction, a continuous extractor has been fabricated for the extraction sequence. This extractor has been found to be acceptable. The particular canister used for the apparatus shown in Figure A-1 contains about 500 g of finished XAD-2. Any size may be constructed; the choice is dependent on the needs of the sampling programs. The XAD-2 is held under light spring tension between a pair of coarse and fine screens. Spacers under the bottom screen allow for even distribution of clean solvent. The three-necked flask should be of sufficient size (3-liter in this case) to hold solvent

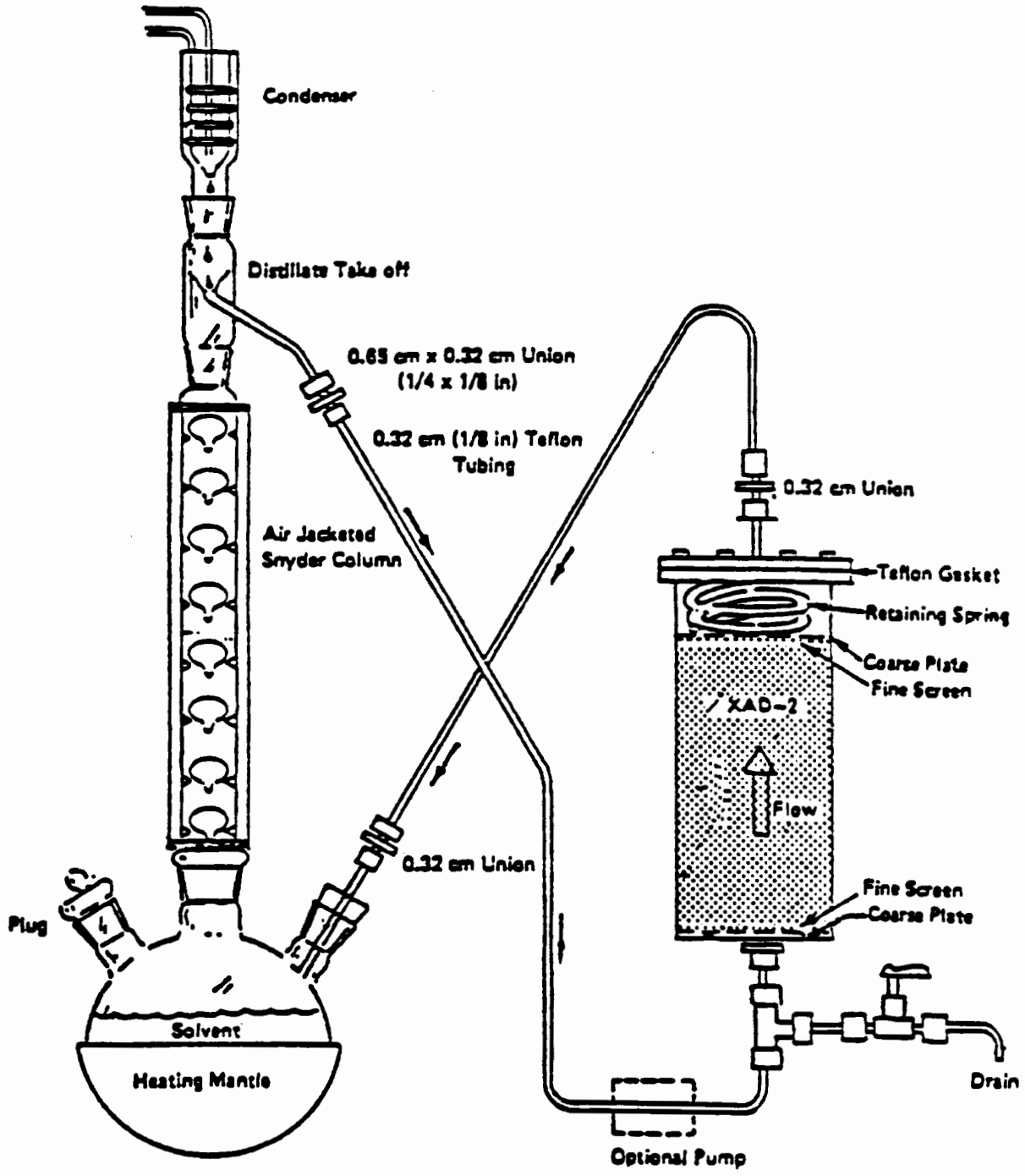


Figure A-1. XAD-2 cleanup extraction apparatus.

equal to twice the dead volume of the XAD-2 canister. Solvent is refluxed through the Snyder column, and the distillate is continuously cycled up through the XAD-2 for extraction and returned to the flask. The flow is maintained upward through the XAD-2 to allow maximum solvent contact and prevent channeling. A valve at the bottom of the canister allows removal of solvent from the canister between changes.

2.2.2 Experience has shown that it is very difficult to cycle sufficient water in this mode. Therefore the aqueous rinse is accomplished by simply flushing the canister with about 20 liters of distilled water. A small pump may be useful for pumping the water through the canister. The water extraction should be carried out at the rate of about 20-40 mL/min.

2.2.3 After draining the water, subsequent methyl alcohol and methylene chloride extractions are carried out using the refluxing apparatus. An overnight or 10- to 20-hr period is normally sufficient for each extraction.

2.2.4 All materials of construction are glass, Teflon, or stainless steel. Pumps, if used, should not contain extractable materials. Pumps are not used with methanol and methylene chloride.

3.0 DRYING

3.1 After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proved to be the fastest and most reliable drying method.

3.2 A simple column with suitable retainers, as shown in Figure A-2, will serve as a satisfactory column. A 10.2-cm (4-in.) Pyrex pipe 0.6 m (2 ft) long will hold all of the XAD-2 from the extractor shown in Figure A-1 or the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum resin load at the exit of the column.

3.3 Method 1: The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has routinely proved to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95-cm (3/8-in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried overnight by consuming a full 160-liter cylinder of liquid nitrogen.

3.4 Method 2: As a second choice, high-purity tank nitrogen may be used to dry the XAD-2. The high-purity nitrogen must first be passed through a bed

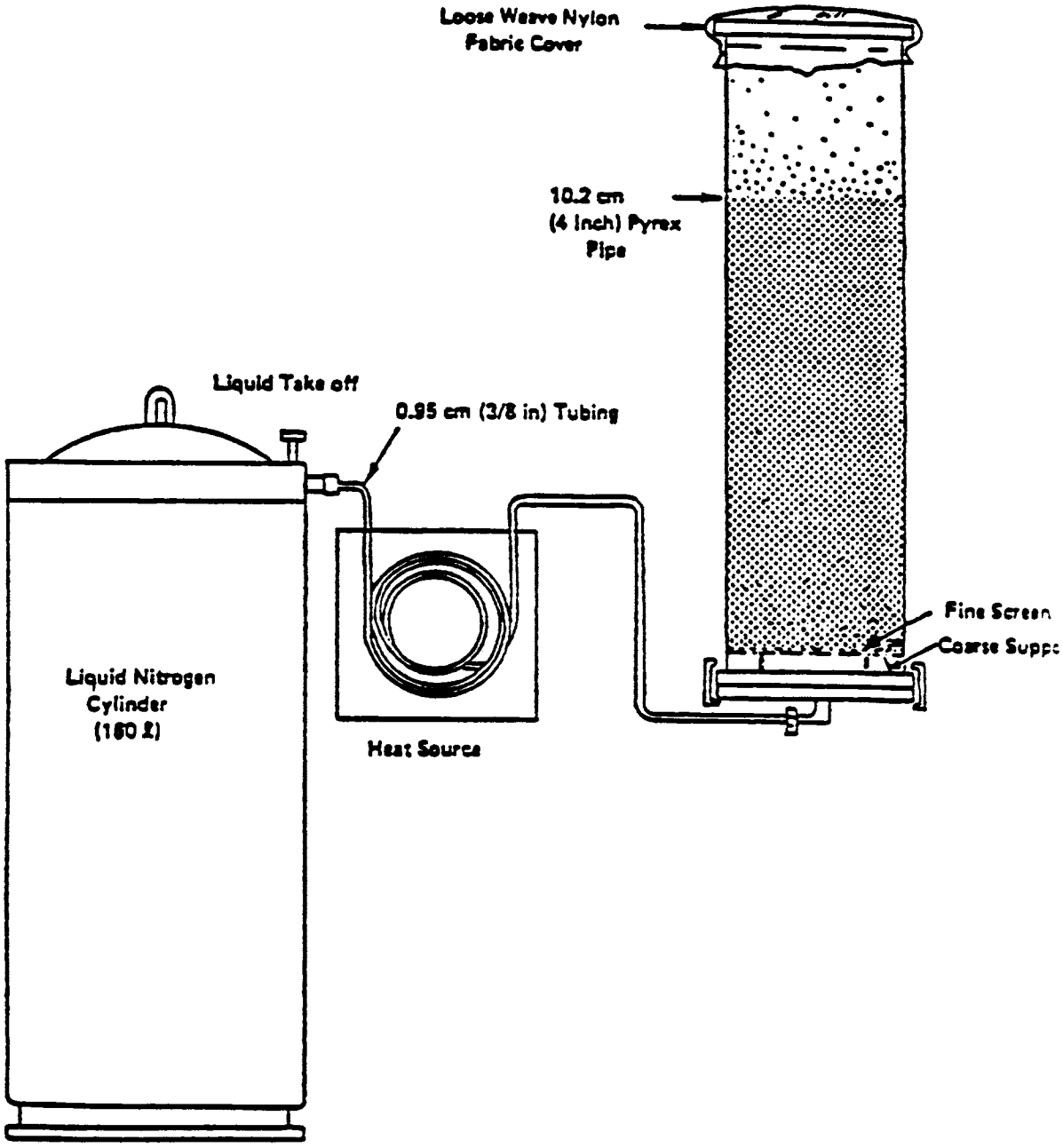


Figure A-2. XAD-2 fluidized-bed drying apparatus.

of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidization may cause the particles to break up.

4.0 QUALITY CONTROL PROCEDURES

4.1 For both Methods 1 and 2, the quality control results must be reported for the batch. The batch must be reextracted if the residual extractable organics are >20 ug/mL by TCO analysis or the gravimetric residue is >0.5 mg/20 g XAD-2 extracted. (See also section 5.1, Method 0010.)

4.2 Four control procedures are used with the final XAD-2 to check for (1) residual methylene chloride, (2) extractable organics (TCO), (3) specific compounds of interest as determined by GC/MS, as described in Section 4.5 below, and (4) residue (GRAV).

4.3 Procedure for residual methylene chloride:

4.3.1 **Description:** A 1±0.1-g sample of dried resin is weighed into a small vial, 3 mL of toluene are added, and the vial is capped and well shaken. Five uL of toluene (now containing extracted methylene chloride) are injected into a gas chromatograph, and the resulting integrated area is compared with a reference standard. The reference solution consists of 2.5 uL of methylene chloride in 100 mL of toluene, simulating 100 ug of residual methylene chloride on the resin. The acceptable maximum content is 1,000 ug/g resin.

4.3.2 **Experimental:** The gas chromatograph conditions are as follows:

6-ft x 1/8-in. stainless steel column containing 10% OV-101 on 100/120 Supelcoport;

Helium carrier at 30 mL/min;

FID operated on 4 x 10^{-11} A/mV;

Injection port temperature: 250°C;

Detector temperature: 305°C;

Program: 30°C(4 min) 40°C/min 250°C (hold); and

Program terminated at 1,000 sec.

4.4 Procedure for residual extractable organics:

4.4.1 **Description:** A 20±0.1-g sample of cleaned, dried resin is weighed into a precleaned alundum or cellulose thimble which is plugged with cleaned glass wool. (Note that 20 g of resin will fill a thimble, and the

resin will float out unless well plugged.) The thimble containing the resin is extracted for 24 hr with 200-mL of pesticide- grade methylene chloride (Burdick and Jackson pesticide-grade or equivalent purity). The 200-mL extract is reduced in volume to 10-mL using a Kuderna-Danish concentrator and/or a nitrogen evaporation stream. Five uL of that solution are analyzed by gas chromatography using the TCO analysis procedure. The concentrated solution should not contain >20 ug/mL of TCO extracted from the XAD-2. This is equivalent to 10 ug/g of TCO in the XAD-2 and would correspond to 1.3 mg of TCO in the extract of the 130-g XAD-2 module. Care should be taken to correct the TCO data for a solvent blank prepared (200 mL reduced to 10 mL) in a similar manner.

4.4.2 **Experimental:** Use the TCO analysis conditions described in the revised Level 1 manual (EPA 600/7-78-201).

4.5 GC/MS Screen: The extract, as prepared in paragraph 4.4.1, is subjected to GC/MS analysis for each of the individual compounds of interest. The GC/MS procedure is described in Chapter Four, Method 8270. The extract is screened at the MDL of each compound. The presence of any compound at a concentration >25 ug/mL in the concentrated extract will require the XAD-2 to be recleaned by repeating the methylene chloride step.

4.6 Methodology for residual gravimetric determination: After the TCO value and GC/MS data are obtained for the resin batch by the above procedures, dry the remainder of the extract in a tared vessel. There must be <0.5 mg residue registered or the batch of resin will have to be extracted with fresh methylene chloride again until it meets this criterion. This level corresponds to 25 ug/g in the XAD-2, or about 3.25 mg in a resin charge of 130 g.

TOTAL CHROMATOGRAPHABLE ORGANIC MATERIAL ANALYSIS

1.0 SCOPE AND APPLICATION

1.1 In this procedure, gas chromatography is used to determine the quantity of lower boiling hydrocarbons (boiling points between 90° and 300°C) in the concentrates of all organic solvent rinses, XAD-2 resin and LC fractions - when Method 1 is used (see References, Method 0010) - encountered in Level 1 environmental sample analyses. Data obtained using this procedure serve a twofold purpose. First, the total quantity of the lower boiling hydrocarbons in the sample is determined. Then whenever the hydrocarbon concentrations in the original concentrates exceed 75 ug/m^3, the chromatography results are reexamined to determine the amounts of individual species.

The extent of compound identification is limited to representing all materials as normal alkanes based upon comparison of boiling points. Thus the method is not qualitative. In a similar manner, the analysis is semiquantitative; calibrations are prepared using only one hydrocarbon. They are replicated but samples routinely are not.

1.2 Application: This procedure applies solely to the Level 1 C7-C16 gas chromatographic analysis of concentrates of organic extracts, neat liquids, and of LC fractions. Throughout the procedure, it is assumed the analyst has been given a properly prepared sample.

1.3 Sensitivity: The sensitivity of this procedure, defined as the slope of a plot of response versus concentration, is dependent on the instrument and must be verified regularly. TRW experience indicates the nominal range is of the order of 77 uV·V·sec·uL/ng of n-heptane and 79 uV·sec·ul/ng of n-hexadecane. The instrument is capable of perhaps one hundredfold greater sensitivity. The level specified here is sufficient for Level 1 analysis.

1.4 Detection limit: The detection limit of this procedure as written is 1.3 ng/uL for a 1 uL injection of n-decane. This limit is arbitrarily based on defining the minimum detectable response as 100 uv·sec. This is an easier operational definition than defining the minimum detection limit to be that amount of material which yields a signal twice the noise level.

1.5 Range: The range of the procedure will be concentrations of 1.3 ng/uL and greater.

1.6 Limitations

1.6.1 **Reporting limitations:** It should be noted that a typical environmental sample will contain compounds which: (a) will not elute in the specified boiling ranges and thus will not be reported, and/or (b)

will not elute from the column at all and thus will not be reported. Consequently, the organic content of the sample as reported is a lower bound and should be regarded as such.

1.6.2 **Calibration limitations:** Quantitation is based on calibration with n-decane. Data should therefore be reported as, e.g., mg C8/m^3 as n-decane. Since response varies linearly with carbon number (over a wide range the assumption may involve a 20% error), it is clear that heptane (C7) detected in a sample and quantitated as decane will be overestimated. Likewise, hexadecane (C16) quantitated as decane will be underestimated. From previous data, it is estimated the error involved is on the order of 6-7%.

1.6.3 **Detection limitations:** The sensitivity of the flame ionization detector varies from compound to compound. However, n-alkanes have a greater response than other classes. Consequently, using an n-alkane as a calibrant and assuming equal responses of all other compounds tends to give low reported values.

2.0 SUMMARY OF METHOD

2.1 A mL aliquot of all 10-mL concentrates is disbursed for GC-TCO analysis. With boiling point-retention time and response-amount calibration curves, the data (peak retention times and peak areas) are interpreted by first summing peak areas in the ranges obtained from the boiling point-retention time calibration. Then, with the response-amount calibration curve, the area sums are converted to amounts of material in the reported boiling point ranges.

2.2 After the instrument is set up, the boiling point-retention time calibration is effected by injecting a mixture of n-C7 through n-C16 hydrocarbons and operating the standard temperature program. Response-quantity calibrations are accomplished by injecting n-decane in n-pentane standards and performing the standard temperature program.

2.3 Definitions

2.3.1 **GC:** Gas chromatography or gas chromatograph.

2.3.2 **C7-C16 n-alkanes:** Heptane through hexadecane.

2.3.3 **GCA temperature program:** 4 min isothermal at 60°C, 10°C/min from 60° to 220°C.

2.3.4 **TRW temperature program:** 5 min isothermal at room temperature, then program from 30°C to 250°C at 15°C/min.

3.0 INTERFERENCES

Not applicable.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: This procedure is intended for use on a Varian 1860 gas chromatograph, equipped with dual flame ionization detectors and a linear temperature programmer. Any equivalent instrument can be used provided that electrometer settings, etc., be changed appropriately.

4.2 Gases:

4.2.1 **Helium:** Minimum quality is reactor grade. A 4A or 13X molecular sieve drying tube is required. A filter must be placed between the trap and the instrument. The trap should be recharged after every third tank of helium.

4.2.2 **Air:** Zero grade is satisfactory.

4.2.3 **Hydrogen:** Zero grade.

4.3 Syringe: Syringes are Hamilton 701N, 10 uL, or equivalent.

4.4 Septa: Septa will be of such quality as to produce very low bleed during the temperature program. An appropriate septum is Supelco Microsep 138, which is Teflon-backed. If septum bleed cannot be reduced to a negligible level, it will be necessary to install septum swingers on the instrument.

4.5 Recorder: The recorder of this procedure must be capable of not less than 1 mV full-scale display, a 1-sec time constant and 0.5 in. per min chart rate.

4.6 Integrator: An integrator is required. Peak area measurement by hand is satisfactory but too time-consuming. If manual integration is required, the method of "height times width at half height" is used.

4.7 Columns:

4.7.1 **Preferred column:** 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-101 on 100/120 mesh Supelcoport.

4.7.2 **Alternate column:** 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-1 (or other silicon phase) on 100/120 mesh Supelcoport.

4.8 Syringe cleaner: Hamilton syringe cleaner or equivalent connected to a suitable vacuum source.

5.0 REAGENTS

5.1 Pentane: "Distilled-in-Glass" (reg. trademark) or "Nanograde" (reg. trademark) for standards and for syringe cleaning.

5.2 Methylene chloride: "Distilled-in-Glass" (reg. trademark) or "Nanograde" (reg. trademark) for syringe cleaning.

6.0 SAMPLING HANDLING AND PRESERVATION

6.1 The extracts are concentrated in a Kuderna-Danish evaporator to a volume less than 10 mL. The concentrate is then quantitatively transferred to a 10-mL volumetric flask and diluted to volume. A 1-mL aliquot is taken for both this analysis and possible subsequent GC/MS analysis and set aside in the sample bank. For each GC-TCO analysis, obtain the sample sufficiently in advance to allow it to warm to room temperature. For example, after one analysis is started, return that sample to the sample bank and take the next sample.

7.0 PROCEDURES

7.1 Setup and checkout: Each day, the operator will verify the following:

7.1.1 That supplies of carrier gas, air and hydrogen are sufficient, i.e., that each tank contains > 100 psig.

7.1.2 That, after replacement of any gas cylinder, all connections leading to the chromatograph have been leak-checked.

7.1.3 That the carrier gas flow rate is 30 $\pm$ 2 mL/min, the hydrogen flow rate is 30 $\pm$ 2 mL/min, and the air flow rate is 300 $\pm$ 20 mL/min.

7.1.4 That the electrometer is functioning properly.

7.1.5 That the recorder and integrator are functioning properly.

7.1.6 That the septa have been leak-checked (leak-checking is effected by placing the soap bubble flow meter inlet tube over the injection port adaptors), and that no septum will be used for more than 20 injections.

7.1.7 That the list of samples to be run is ready.

7.2 Retention time calibration:

7.2.1 To obtain the temperature ranges for reporting the results of the analyses, the chromatograph is given a normal boiling point-retention time calibration. The n-alkanes, their boiling points, and data reporting ranges are given in the table below:

	NBP, °C	Reporting Range, °C	Report As
n-heptane	98	90-110	C7
n-octane	126	110-140	C8
n-nonane	151	140-160	C9
n-decane	174	160-180	C10
n-undecane	194	180-200	C11
n-dodecane	214	200-220	C12
n-tridecane	234	220-240	C13
n-tetradecane	252	240-260	C14
n-pentadecane	270	260-280	C15
n-hexadecane	288	280-300	C16

7.2.2 **Preparation of standards:** Preparing a mixture of the C7-C16 alkanes is required. There are two approaches: (1) use of a standards kit (e.g., Polyscience Kit) containing bottles of mixtures of selected n-alkanes which may be combined to produce a C7-C16 standard; or (2) use of bottles of the individual C7-C16 alkanes from which accurately known volumes may be taken and combined to give a C7-C16 mixture.

7.2.3 **Procedure for retention time calibration:** This calibration is performed at the start of an analytical program; the mixture is chromatographed at the start of each day. To attain the required retention time precision, both the carrier gas flow rate and the temperature program specifications must be observed. Details of the procedure depend on the instrument being used. The general procedure is as follows:

7.2.3.1 Set the programmer upper limit at 250°C. If this setting does not produce a column temperature of 250°C, find the correct setting.

7.2.3.2 Set the programmer lower limit at 30°C.

7.2.3.3 Verify that the instrument and samples are at room temperature.

7.2.3.4 Inject 1 uL of the n-alkane mixture.

7.2.3.5 Start the integrator and recorder.

7.2.3.6 Allow the instrument to run isothermally at room temperature for five min.

7.2.3.7 Shut the oven door.

7.2.3.8 Change the mode to Automatic and start the temperature program.

7.2.3.9 Repeat Steps 1-9 a sufficient number of times so that the relative standard deviation of the retention times for each peak is <5%.

7.3 Response calibration:

7.3.1 For the purposes of a Level 1 analysis, response-quantity calibration with n-decane is adequate. A 10-uL volume of n-decane is injected into a tared 10 mL volumetric flask. The weight injected is obtained and the flask is diluted to the mark with n-pentane. This standard contains about 730 ng n-decane per uL n-pentane. The exact concentration depends on temperature, so that a weight is required. Two serial tenfold dilutions are made from this standard, giving standards at about 730, 73, and 7.3 ng n-decane per uL n-pentane, respectively.

7.3.2 **Procedure for response calibration:** This calibration is performed at the start of an analytical program and monthly thereafter. The most concentrated standard is injected once each day. Any change in calibration necessitates a full calibration with new standards. Standards are stored in the refrigerator locker and are made up monthly.

7.3.2.1 Verify that the instrument is set up properly.

7.3.2.2 Set electrometer at 1×10^{-10} A/mV.

7.3.2.3 Inject 1 uL of the highest concentration standard.

7.3.2.4 Run standard temperature program as specified above.

7.3.2.5 Clean syringe.

7.3.2.6 Make repeated injections of all three standards until the relative standard deviations of the areas of each standard are ≤5%.

7.4 Sample analysis procedure:

7.4.1 The following apparatus is required:

7.4.1.1 **Gas chromatograph** set up and working.

7.4.1.2 **Recorder, integrator** working.

7.4.1.3 **Syringe and syringe cleaning apparatus.**

7.4.1.4 **Parameters:** Electrometer setting is 1×10^{-10} A/mV; recorder is set at 0.5 in./min and 1 mV full-scale.

7.4.2 Steps in the procedure are:

7.4.2.1 Label chromatogram with the data, sample number, etc.

7.4.2.2 Inject sample.

7.4.2.3 Start integrator and recorder.

7.4.2.4 After isothermal operation for 5 min, begin temperature program.

7.4.2.5 Clean syringe.

7.4.2.6 Return sample; obtain new sample.

7.4.2.7 When analysis is finished, allow instrument to cool. Turn chromatogram and integrator output and data sheet over to data analyst.

7.5 Syringe cleaning procedure:

7.5.1 Remove plunger from syringe.

7.5.2 Insert syringe into cleaner; turn on aspirator.

7.5.3 Fill pipet with pentane; run pentane through syringe.

7.5.4 Repeat with methylene chloride from a separate pipet.

7.5.5 Flush plunger with pentane followed by methylene chloride.

7.5.6 Repeat with methylene chloride.

7.6 Sample analysis decision criterion: The data from the TCO analyses of organic extract and rinse concentrates are first used to calculate the total concentration of C7-C16 hydrocarbon-equivalents (Paragraph 7.7.3) in the sample with respect to the volume of air actually sampled, i.e., ug/m^3. On this basis, a decision is made both on whether to calculate the quantity of each n-alkane equivalent present and on which analytical procedural pathway will be followed. If the total organic content is great enough to warrant continuing the analysis -- >500 ug/m^3 -- a TCO of less than 75 ug/m^3 will require only LC fractionation and gravimetric determinations and IR spectra to be obtained on each fraction. If the TCO is greater than 75 ug/m^3, then the first seven LC fractions of each sample will be reanalyzed using this same gas chromatographic technique.

7.7 Calculations:

7.7.1 **Boiling Point - Retention Time Calibration:** The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.1.1 Average the retention times and calculate relative standard deviations for each n-hydrocarbon.

7.7.1.2 Plot average retention times as abscissae versus normal boiling points as ordinates.

7.7.1.3 Draw in calibration curve.

7.7.1.4 Locate and record retention times corresonding to boiling ranges 90-100, 110-140, 140-160, 160-180, 180-200, 200-220, 220-240, 240-260, 260-280, 280-300°C.

7.7.2 **Response-amount calibration:** The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.2.1 Average the area responses of each standard and calculate relative standard deviations.

7.7.2.2 Plot response (uv·sec) as ordinate versus ng/uL as abscissa.

7.7.2.3 Draw in the curve. Perform least squares regression and obtain slope (uV·sec·uL/ng).

7.7.3 **Total C7-C16 hydrocarbons analysis:** The required data for this calculation are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.3.1 Sum the areas of all peaks within the retention time range of interest.

7.7.3.2 Convert this area (uV·sec) to ng/uL by dividing by the weight response for n-decane (uV·sec.uL/ng).

7.7.3.3 Multiply this weight by the total concentrate volume (10 mL) to get the weight of the C7-C16 hydrocarbons in the sample.

7.7.3.4 Using the volume of gas sampled or the total weight of sample acquired, convert the result of Step 7.7.3.3 above to ug/m^3.

7.7.3.5 If the value of total C7-C16 hydrocarbons from Step 7.7.3.4 above exceeds 75 ug/m^3, calculate individual hydrocarbon concentrations in accordance with the instructions in Paragraph 7.7.5.5 below.

7.7.4 **Individual C7-C16 n-Alkane Equivalent Analysis:** The required data from the analyses are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.4.1 Sum the areas of peaks in the proper retention time ranges.

7.7.4.2 Convert areas (uV·sec) to ng/uL by dividing by the proper weight response (uV·sec·uL/ng).

7.7.4.3 Multiply each weight by total concentrate volume (10 mL) to get weight of species in each range of the sample.

7.7.4.4 Using the volume of gas sampled on the total weight of sample acquired, convert the result of Step 7.7.4.3 above to ug/m^3.

8.0 QUALITY CONTROL

8.1 Appropriate QC is found in the pertinent procedures throughout the method.

9.0 METHOD PERFORMANCE

9.1 Even relatively comprehensive error propagation analysis is beyond the scope of this procedure. With reasonable care, peak area reproducibility of a standard should be of the order of 1% RSD. The relative standard deviation of the sum of all peaks in a fairly complex waste might be of the order of 5-10%. Accuracy is more difficult to assess. With good analytical technique, accuracy and precision should be of the order of 10-20%.

10.0 REFERENCES

1. Emissions Assessment of Conventional Stationary Combustion Systems: Methods and Procedure Manual for Sampling and Analysis, Interagency Energy/Environmental R&D Program, Industrial Environmental Research Laboratory, Research Triangle Park, NC 27711, EPA-600/7-79-029a, January 1979.

METHOD 0011

SAMPLING FOR SELECTED ALDEHYDE AND KETONE EMISSIONS FROM STATIONARY SOURCES

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of the analytes listed in the following table:

Analyte	CAS No.[a]
Formaldehyde	50-00-0
Acetaldehye	75-07-0
Acetophenone	98-86-2
Isophorone	78-59-1
Propionaldehyde	123-38-6

[a] Chemical Abstract Service Registry Number

This method has been applied specifically to the above analytes. Many laboratories have extended method application to other aldehydes and ketones. This method is possibly applicable to other aldehydes and ketones from stationary sources as specified in the regulations. However, this method is not applicable to quinone (CAS No. 106-51-4), acrolein (CAS No. 107-02-08), methyl ethyl ketone (CAS No. 78-93-3), and methyl isobutyl ketone (CAS No. 108-10-1).

1.2 The detection limit for a 30 ft^3 (849 L) sample over a 1 hour sampling period may be as low as 10 ppbv for acetophenone and isophorone, 60 ppbv for propionaldehyde, 40 ppbv for acetaldehyde, and 90 ppbv for formaldehyde. Because the derivatization reaction is based on the formation of an equilibrium state between reactants and products, for some compounds quantitative recoveries may not be achieved until the concentration exceeds 200 ppbv.

1.3 This method is restricted to use by, or under the close supervision of, analysts experienced in sampling organic compounds in air. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in aqueous acidic 2,4-dinitrophenylhydrazine. Formaldehyde present in the emissions reacts with the 2,4-dinitrophenylhydrazine to form the formaldehyde dinitrophenylhydrazone derivative. The dinitrophenylhydrazone derivative is extracted, solvent-exchanged, concentrated, and then analyzed by high performance liquid chromatography (HPLC) according to Method 8315 or other appropriate technique.

3.0 INTERFERENCES

3.1 A decomposition product of 2,4-dinitrophenylhydrazine, 2,4-dinitroaniline, can be an analytical interferant if concentrations are high. The 2,4-dinitroaniline can coelute with the 2,4-dinitrophenylhydrazone of formaldehyde under the high performance liquid chromatography conditions used for the analysis. High concentrations of highly oxygenated compounds, especially acetone, that have the same retention time or nearly the same retention time as the dinitrophenylhydrazone of formaldehyde, and that also absorb at 360 nm, will interfere with the analysis.

3.2 Formaldehyde, acetone, and 2,4-dinitroaniline contamination of the aqueous acidic 2,4-dinitrophenylhydrazine (DNPH) reagent is frequently encountered. The reagent must be prepared within five days of use in the field and must be stored in an uncontaminated environment both before and after sampling, in order to minimize blank problems. Some concentration of acetone contamination is unavoidable, because acetone is ubiquitous in laboratory and field operations. However, the acetone contamination must be minimized.

3.3 Dimethylolurea creates a slight positive interference; and hexamethylenetetramine and paraformaldehyde significantly interfere with the determination of formaldehyde. These compounds can decompose in the acidic reagent used to collect the sample to form formaldehyde;

3.4 Tolualdehyde interferes with the determination of acetophenone because they coelute chromatographically;

3.5 High levels of nitrogen dioxide can interfere by consuming all of the reagent.

4.0 APPARATUS AND MATERIALS

4.1 This sampling train configuration is adapted from Method 5 (see Ref. 1) procedures. The sampling train consists of the following components: Probe nozzle, pitot tube, differential pressure gauge, metering system, barometer, and gas density determination equipment. A schematic of the sampling train is shown in Figure 1.

4.1.1 Probe Nozzle - The probe nozzle shall be quartz or glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant inner diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32 to 1.27 cm (1/8 to ½ in.), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Sec. 8.1.

4.1.2 Probe Liner - Borosilicate glass or quartz shall be used for the probe liner. The tester should not allow the temperature in the probe to exceed 120 ±14°C (248 ±25°F).

4.1.3 Pitot Tube - The pitot tube shall be Type S or any other appropriate device. The Type S pitot tube shall be made of metal tubing (e.g., stainless steel). It is recommended that the external tubing diameter be between 0.48 and 0.95 cm. There shall be an equal distance from the base of each leg to its face-opening plane; it is recommended that this distance be between 1.05 and 1.50 times the external tubing diameter. The face openings of the pitot tube shall, preferably, be aligned but slight misalignments of the openings are permissible. The

Type S pitot tube assembly shall have a known coefficient, determined as outlined in Method 2 (see Ref. 1). The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2) during sampling.

4.1.4 Differential Pressure Gauge - The differential pressure gauge shall be an inclined manometer or equivalent device as described in Method 2. One manometer shall be used for velocity-head readings and the other for orifice differential pressure readings.

4.1.5 Impingers - The sampling train requires a minimum of five impingers, connected as shown in Figure 1, with ground glass (or equivalent) vacuum-tight fittings. For the first, third, fourth, and fifth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.27 cm (½ in) inside diameter glass tube extending to 1.27 cm (½ in.) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. Place a thermometer capable of measuring temperature to within 1°C (2°F) at the outlet of the fifth impinger for monitoring purposes.

4.1.6 Metering System - The necessary components of the metering system are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1%, and related equipment as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems may be used which are capable of maintaining sample volumes to within 2%. The metering system may be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

4.1.7 Barometer - The barometer may be mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service Station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase (vice versa for elevation decrease).

4.1.8 Gas Density Determination Equipment - The gas density determination equipment includes a temperature sensor and pressure gauge (as described in Method 2) and gas analyzer, if necessary (an Orsat of Fyrite type combustion gas analyzer, or equivalent. For analyzer maintenance and operation procedures, follow the instructions recommended by the manufacturer). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

4.2 Sample Recovery

4.2.1 Probe Liner - Probe nozzle and brushes; Teflon® bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel,

Teflon®, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the impingers.

4.2.2 Wash Bottles - Three wash bottles are required. Teflon® or glass wash bottles are recommended. Polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to the organic solvents used for sample recovery.

4.2.3 Graduated Cylinder and/or Balance - A graduated cylinder or balance is required to measure condensed water to the nearest 1 mL or 1 g. Graduated cylinders shall have divisions not greater than 2 mL. Laboratory balances capable of weighing to ±0.5 g are required.

4.2.4 Amber Glass Storage Containers - One-liter wide-mouth amber flint glass bottles with Teflon®-lined caps are required to store impinger water samples. The bottles must be sealed with Teflon® tape.

4.2.5 Rubber Policeman and Funnel - A rubber policeman and funnel are required to aid in the transfer of materials into and out of containers in the field.

4.3 Reagent Preparation

4.3.1 Bottles/Caps - Amber 1 - 4 L bottles with Teflon®-lined caps are required for storing cleaned DNPH solution. Additional 4-L bottles are required to collect waste organic solvents.

4.3.2 Large Glass Container - At least one large glass (8 to 16 L) is required for mixing the aqueous acidic DNPH solution.

4.3.3 Stir Plate/Large Stir Bars/Stir Bar Retriever - A magnetic stir plate and large stir bar are required for the mixing of the aqueous acidic DNPH solution. A stir bar retriever is needed for removing the stir bar from the large container holding the DNPH solution.

4.3.4 Buchner Filter/Filter Flask/Filter Paper - A large filter flask (2-4 L) with a buchner filter, appropriate rubber stopper, filter paper, and connecting tubing are required for filtering the aqueous acidic DNPH solution prior to cleaning.

4.3.5 Separatory Funnel - At least one large separatory funnel (2 L) is required for cleaning the DNPH prior to use.

4.3.6 Beakers - Beakers (150 mL, 250 mL, and 400 mL) are useful for holding/measuring organic liquids when cleaning the aqueous acidic DNPH solution and for weighing DNPH crystals.

4.3.7 Funnels - At least one large funnel is needed for pouring the aqueous acidic DNPH into the separatory funnel.

4.3.8 Graduated Cylinders - At least one large graduated cylinder (1 to 2 L) is required for measuring organic-free reagent water and acid when preparing the DNPH solution.

4.3.9 Top-loading Balance - A one-place top loading balance is needed for weighing out the DNPH crystals used to prepare the aqueous acidic DNPH solution.

4.3.10 Spatulas - Spatulas are needed for weighing out DNPH when preparing the aqueous DNPH solution.

4.4 Crushed Ice - Quantities of crushed ice ranging from 10-50 lb may be necessary during a sampling run, depending upon ambient temperature. Samples which have been taken must be stored and shipped cold; sufficient ice for this purpose must be allowed.

5.0 REAGENTS

5.1 Reagent Grade Chemicals - Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free Reagent Water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Silica Gel - Silica gel shall be indicating type, 6-16 mesh. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

5.4 2,4-Dinitrophenylhydrazine (DNPH), $[2,4\text{-}(0_2N)_2C_6H_3]NHNH_2$ - The quantity of water may vary from 10 to 30%.

5.4.1 The 2,4-dinitrophenylhydrazine reagent must be prepared in the laboratory within five days of sampling use in the field. Preparation of DNPH can also be done in the field, with consideration of appropriate procedures required for safe handling of solvent in the field. When a container of prepared DNPH reagent is opened in the field, the contents of the opened container should be used within 48 hours. All laboratory glassware must be washed with detergent and water and rinsed with water, methanol, and methylene chloride prior to use.

NOTE: DNPH crystals and DNPH solution are potential carcinogens and should be handled with plastic gloves at all times, with prompt and extensive use of running water in case of skin exposure.

5.4.2 Preparation of Aqueous Acidic DNPH Derivatizing Reagent - Each batch of DNPH reagent should be prepared and purified within five days of sampling, according to the procedure described below.

NOTE: Reagent bottles for storage of cleaned DNPH derivatizing solution must be rinsed with acetonitrile and dried before use. Baked glassware is not essential for preparation of DNPH reagent. The glassware must not be rinsed with acetone or an unacceptable concentration of acetone contamination will be introduced. If field preparation of DNPH is performed, caution must be exercised in avoiding acetone contamination.

5.4.2.1 Place an 8 L container under a fume hood on a magnetic stirrer. Add a large stir bar and fill the container half full of organic-free reagent water. Save the

empty bottle from the organic-free reagent water. Start the stirring bar and adjust the stir rate to be as fast as possible. Using a graduated cylinder, measure 1.4 L of concentrated hydrochloric acid. Slowly pour the acid into the stirring water. Fumes may be generated and the water may become warm. Weigh the DNPH crystals to ±0.1 g (see Table 1 for approximate amounts) and add to the stirring acid solution. Fill the 8 L container to the 8 L mark with organic-free reagent water and stir overnight. If all of the DNPH crystals have dissolved overnight, add additional DNPH and stir for two more hours. Continue the process of adding DNPH with additional stirring until a saturated solution has been formed, as evidenced by the presence of visible crystals after continued stirring. Filter the DNPH solution using vacuum filtration. Gravity filtration may be used, but a much longer time is required. Store the filtered solution in an amber bottle at room temperature.

5.4.2.2 Within five days of proposed use, place about 1.6 L of the DNPH reagent in a 2 L separatory funnel. Add approximately 200 mL of methylene chloride and stopper the funnel. Wrap the stopper of the funnel with paper towels to absorb any leakage. Invert and vent the funnel. Then shake vigorously for 3 minutes. Initially, the funnel should be vented frequently (every 10 - 15 seconds). After the layers have separated, discard the lower (organic) layer.

5.4.2.3 Extract the DNPH a second time with methylene chloride and finally with cyclohexane. When the cyclohexane layer has separated from the DNPH reagent, the cyclohexane layer will be the top layer in the separatory funnel. Drain the lower layer (the cleaned extracted DNPH reagent solution) into an amber bottle that has been rinsed with acetonitrile and allowed to dry.

5.4.3 DNPH Reagent Check - Take two aliquots of the extracted DNPH reagent. The size of the aliquots is dependent upon the exact sampling procedure used, but 100 mL is reasonably representative. Analyze one aliquot of the reagent according to Sec. 7 of Method 8315 as a Quality Control check to ensure that the background in the reagent is acceptable for field use. Save the other aliquot of aqueous acidic DNPH for use as a method blank when the analysis is performed. The reagent is acceptable for use if the background meets the AIC (Acceptable Impurity Concentration) as specified in Sec. 5.4.5.

5.4.4 Shipment to the Field - Tightly cap the bottle containing extracted DNPH reagent using a Teflon®-lined cap. Seal the bottle with Teflon® tape. After the bottle is labeled, the bottle may be placed in a friction-top can (paint can or equivalent) containing a 1-2 inch layer of granulated charcoal and stored at ambient temperature until use.

5.4.4.1 If the DNPH reagent has passed the Quality Control criteria, the reagent may be packaged to meet necessary shipping requirements and sent to the sampling area. If the Quality Control criteria are not met, the reagent solution may be re-extracted or the solution may be re-prepared and the extraction sequence repeated.

5.4.4.2 If the DNPH reagent is not used in the field within five days of extraction, an aliquot may be taken and analyzed as described in Sec. 7 of Method 8315. If the reagent meets the Quality Control requirements, the reagent may be used. If the reagent does not meet the Quality Control requirements, the reagent must be discarded and new reagent must be prepared and tested.

5.4.5 Calculation of Acceptable Concentrations of Impurities in DNPH Reagent - The acceptable impurity concentration (AIC, µg/mL) is calculated from the expected analyte concentration in the sampled gas (EAC, ppbv), the volume of air that will be sampled at standard conditions (SVOL, L), the formula weight of the analyte (FW, g/mol), and the volume of DNPH reagent that will be used in the impingers (RVOL, mL):

$$AIC = 0.1 \times [EAC \times SVOL \times FW/24.4 \times (FW + 180)/FW](RVOL/1{,}000)$$

where:

0.1 is the acceptable contaminant concentration,
24.4 is a factor relating ppbv to g/L,
180 is a factor relating underivatized to derivatized analyte, and
1,000 is a unit conversion factor.

5.4.6 Disposal of Excess DNPH Reagent - Excess DNPH reagent may be returned to the laboratory and recycled or treated as aqueous waste for disposal purposes. 2,4-Dinitrophenylhydrazine is a flammable solid when dry, so water should not be evaporated from the solution of the reagent.

5.5 Field Spike Standard Preparation - To prepare a formaldehyde field spiking standard at 4010 mg/L, use a 500 µL syringe to transfer 0.5 mL of 37% by weight of formaldehyde (401 g/L) to a 50 mL volumetric flask containing approximately 40 mL of methanol. Dilute to 50 mL with methanol.

5.6 Hydrochloric Acid, HCl - Reagent grade hydrochloric acid (approximately 12N) is required for acidifying the aqueous DNPH solution.

5.7 Methylene Chloride, CH_2Cl_2 - Methylene chloride (suitable for residue and pesticide analysis, GC/MS, HPLC, GC, Spectrophotometry or equivalent) is required for cleaning the aqueous acidic DNPH solution, rinsing glassware, and recovery of sample trains.

5.8 Cyclohexane, C_6H_{12} - Cyclohexane (HPLC grade) is required for cleaning the aqueous acidic DNPH solution.

NOTE: Do not use spectroanalyzed grades of cyclohexane if this sampling methodology is extended to aldehydes and ketones with four or more carbon atoms.

5.9 Methanol, CH_3OH - Methanol (HPLC grade or equivalent) is necessary for rinsing glassware.

5.10 Acetonitrile, CH_3CN - Acetonitrile (HPLC grade or equivalent) is required for rinsing glassware.

5.11 Formaldehyde, HCHO - Formaldehyde (analytical reagent grade, or equivalent) is required for preparation of standards. If other aldehydes or ketones are used, analytical reagent grade, or equivalent, is required.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

6.2 Laboratory Preparation

6.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD-0576 (Air Pollution Technical Document, see references), unless otherwise specified.

6.2.2 Weigh several 200 to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

6.3 Preliminary Field Determinations

6.3.1 Select the sampling site and the minimum number of sampling points according to Method 1 (see Ref. 1) or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using Method 2. A leak-check of the pitot lines according to Method 2 must be performed. Determine the stack gas moisture content using Approximation Method 4 (see Ref. 1) or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack gas dry molecular weight, as described in Method 2. If integrated Method 3 (see Ref. 1) sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

6.3.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 L/min (1.0 cfm). During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Sec. 2 of Method 2).

6.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

6.3.4 A minimum of 45 ft^3 of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of formaldehyde from incineration systems (45 ft^3 is equivalent to one hour of sampling at 0.75 dscf). Additional sample volume shall be collected as necessitated by the capacity of the DNPH reagent and analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in Sec. 10.0.

6.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus 0.5 min.

6.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-volume samples. In these cases, careful documentation must be maintained in order to allow accurate calculation of concentrations.

6.4 Preparation of Collection Train

6.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon® film or aluminum foil until just prior to assembly or until sampling is about to begin.

NOTE: Appendix A at the end of this procedure contains guidance on the addition of a filter as a check on the survival of particulate material through the impinger system. This filter can be added to the impinger train either after the second impinger or after the third impinger.

6.4.2 Place 200 mL of purified DNPH reagent in the first impinger and 100 mL of reagent in the second and third impingers, and leave the fourth impinger empty. Transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger. Care should be taken to ensure that the silica gel is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

6.4.3 With a glass or quartz liner, install the selected nozzle using a Viton-A O-ring when stack temperatures are less than 260°C (500°F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connecting systems utilizing either 316 stainless steel or Teflon® ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

6.4.4 Assemble the train as shown in Figure 1. During assembly, do not use any silicone grease on ground-glass joints upstream of the impingers. Use Teflon® tape, if required. A very light coating of silicone grease may be used on ground-glass joints downstream of the impingers, but the silicone grease should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone grease contamination. If necessary, Teflon® tape may be used to seal leaks. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

6.4.5 Place crushed ice all around the impingers.

6.4.6 Turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize.

6.5 Leak-Check Procedures

6.5.1 Pre-test Leak Check

6.5.1.1 After the sampling train has been assembled, turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to

stabilize. If a Viton-A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381 mm Hg (15 in. Hg) vacuum.

NOTE: A lower vacuum may be used, provided that the lower vacuum is not exceeded during the test.

6.5.1.2 If an asbestos string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first attaching a carbon-filled leak check impinger to the inlet and then plugging the inlet and pulling a 381 mm Hg (15 in. Hg) vacuum. (A lower vacuum may be used if this lower vacuum is not exceeded during the test.) Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum. Alternatively, leak-check the probe with the rest of the sampling train in one step at 381 mm Hg (15 in. Hg) vacuum. Leakage rates no greater than 4% of the average sampling rate or less than or equal to 0.00057 m^3/min (0.02 cfm), whichever is less, are acceptable.

6.5.1.3 The following leak check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with the fine-adjust valve fully open and coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve, as liquid will back up into the train. If the desired vacuum is exceeded, either perform the leak check at this higher vacuum or end the leak check, as shown below, and start over.

6.5.1.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in.) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed to prevent the liquid in the impingers from being forced backward into the sampling line and silica gel from being entrained backward into the third impinger.

6.5.2 Sampling Run Leak Check

6.5.2.1 If, during the sampling run, a component change (i.e., impinger) becomes necessary, a leak check shall be conducted immediately after the interruption of sampling and before the change is made. The leak check shall be done according to the procedure described in Sec. 6.5.1, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester must void the sampling run.

NOTE: Any correction of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

6.5.2.2 Immediately after a component change and before sampling is reinitiated, a leak check similar to a pre-test leak check must also be conducted.

6.5.3 Post-test Leak Check - A leak check is mandatory at the conclusion of each sampling run. The leak check shall be done with the same procedures as the pre-test leak check, except that the post-test leak check shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall record the leakage rate and void the sampling run.

6.6 Sampling Train Operation

6.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, below 28 L/min (1.0 cfm). Maintain a temperature around the probe of 120°C (248° ±25°F).

6.6.2 For each run, record the data on a data sheet such as the one shown in Figure 2. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings required by Figure 2 at least once at each sample point during each time increment and additional readings when significant adjustments (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

6.6.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot tube coefficient is 0.84 ±0.02 and the stack gas equivalent density (dry molecular weight) is equal to 29 ±4. APTD-0576 details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations.

6.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack in order to prevent liquid from backing up through the train. If necessary, the pump may be turned on with the coarse-adjust valve closed.

6.6.5 When the probe is in position, block off the openings around the probe and stack access port to prevent nonrepresentative dilution of the gas stream.

6.6.6 Traverse the stack cross section, as required by Method 1, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

6.6.7 During the test run, make periodic adjustments to keep the temperature around the probe at the proper levels. Add more ice and, if necessary, salt, to maintain a temperature of less than 20°C (68°F) at the silica gel outlet. Also, periodically check the level and zero of the manometer.

6.6.8 A single train shall be used for the entire sampling run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. An additional train or additional trains may also be used for sampling when the capacity of a single train is exceeded.

6.6.9 When two or more trains are used, separate analyses of components from each train shall be performed. If multiple trains have been used because the capacity of a single train would be exceeded, first impingers from each train may be combined, and second impingers from each train may be combined.

6.6.10 At the end of the sampling run, turn off the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak check. Also, leak check the pitot lines as described in Method 2. The lines must pass this leak check in order to validate the velocity-head data.

6.6.11 Calculate percent isokinetic variation (see Method 5) to determine whether the run was valid or another test should be made.

7.0 SAMPLE RECOVERY AND PREPARATION FOR ANALYSIS

7.1 Preparation

7.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling because a vacuum will be created, drawing liquid from the impingers back through the sampling train.

7.1.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet, being careful not to lose any condensate that might be present. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used, let any condensed water or liquid drain into the impingers. Cap off any open impinger inlets and outlets. Ground glass stoppers, Teflon® caps, or caps of other inert materials may be used to seal all openings.

7.1.3 Transfer the probe and impinger assembly to an area that is clean and protected from wind so that the chances of contaminating or losing the sample are minimized.

7.1.4 Inspect the train before and during disassembly, and note any abnormal conditions.

7.1.5 Save a portion of all washing solution (methylene chloride, water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle being used and place each in a separate, pre-labeled sample container.

7.2 Sample Containers

7.2.1 Container 1 - Probe and Impinger Catches. Using a graduated cylinder, measure to the nearest mL, and record the volume of the solution in the first three impingers. Alternatively, the solution may be weighed to the nearest 0.5 g. Transfer the impinger solution from the graduated cylinder into the amber flint glass bottle. Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all surfaces to which the sample is exposed (including the probe nozzle, probe fitting, probe liner, first impinger, and impinger connector) with methylene chloride. Use less than 500 mL for the entire wash (250 mL would be better, if possible). Add the washings to the sample container.

7.2.1.1 Carefully remove the probe nozzle and rinse the inside surface with methylene chloride from a wash bottle. Brush with a Teflon® bristle brush, and rinse until the rinse shows no visible particles or yellow color, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with methylene chloride in a similar way.

7.2.1.2 Rinse the probe liner with methylene chloride. While squirting the methylene chloride into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with methylene chloride. Let the methylene chloride drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Following the rinse with a Teflon® brush. Hold the probe in an inclined position, and squirt methylene chloride into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any methylene chloride, water, and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. Rinse the brush with methylene chloride or water, and quantitatively collect these washings in the sample container. After the brushings, make a final rinse of the probe as described above.

NOTE: Between sampling runs, brushes must be kept clean and free from contamination.

7.2.1.3 Rinse the inside surface of each of the first three impingers (and connecting tubing) three separate times. Use a small portion of methylene chloride for each rinse. Water will be required for the recovery of the impingers in addition to the specified quantity of methylene chloride. There will be at least two phases in the impingers. This two-phase mixture does not pour well, and a significant amount of the impinger catch will be left on the walls. The use of water as a rinse makes the recovery quantitative. Make a final rinse of each surface, using both methylene chloride and water.

7.2.1.4 After all methylene chloride and water washings and particulate matter have been collected in the sample container, tighten the lid so that solvent, water, and DNPH reagent will not leak out when the container is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Seal the container with Teflon® tape. Label the container clearly to identify its contents.

7.2.1.5 If the first two impingers are to be analyzed separately to check for breakthrough, separate the contents and rinses of the two impingers into individual containers. Care must be taken to avoid physical carryover from the first impinger to the second. The formaldehyde hydrazone is a solid which floats and froths on top of the impinger solution. Any physical carryover of collected moisture into the second impinger will invalidate a breakthrough assessment.

7.2.2 Container 2 - Sample Blank. Prepare a sample blank by using an amber flint glass container and adding a volume of DNPH reagent and methylene chloride equal to the total volume in Container 1. Process the blank in the same manner as Container 1.

7.2.3 Container 3 - Silica Gel. Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. The impinger containing the silica gel may be used as a sample transport container with both ends sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon® caps may be used. The silica gel impinger should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If the silica gel is removed from the impinger, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids to transfer the silica gel. If a balance is available in the field, the spent silica gel (or silica gel plus impinger) may be weighed to the nearest 0.5 g.

7.2.4 Sample containers should be placed in a cooler, cooled by although not in contact with ice. Sample containers must be placed vertically and, since they are glass, protected from breakage during shipment. Samples should be cooled during shipment so they will be received cold at the laboratory.

7.3 The dinitrophenylhydrazone derivative is then analyzed by high performance liquid chromatography (HPLC) (Method 8315) or other appropriate technique.

8.0 CALIBRATION

8.1 Probe Nozzle - Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When the nozzles become nicked or corroded, they shall be replaced and calibrated before use. Each nozzle must be permanently and uniquely identified.

8.2 Pitot Tube - The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked or corroded and if it meets design and intercomponent spacing specifications.

8.3 Metering System

8.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to

correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak check be conducted. For metering system having diaphragm pumps, the normal leak check procedure will not detect leakages within the pump. For these cases, the following leak check procedure will apply: make a ten-minute calibration run at 0.00057 m^3/min (0.02 cfm). At the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

8.3.2 After each field use, check the calibration of the metering system by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). Set the vacuum at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

8.3.3 Leak Check of Metering System - The portion of the sampling train from the pump to the orifice meter (see Figure 1) should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the following procedure: Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 - 18 cm (5 - 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks must be corrected.

NOTE: If the dry-gas-meter coefficient values obtained before and after a test series differ by greater than 5%, either the test series must be voided or calculations for test series must be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

8.4 Probe Heater - The probe heating system must be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

8.5 Temperature Gauges - Each thermocouple must be permanently and uniquely marked on the casting. All mercury-in-glass reference thermometers must conform to ASTM E-1 63C or 63F (American Society for Testing and Materials) specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at the ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change greater than 1.5%.

8.5.1 Impinger and Dry-gas Meter Thermocouples - For the thermocouples used to measure the temperature of the gas leaving the impinger train, a three-point calibration at ice water, room air, and boiling water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ±2°C (3.6°F) with those of the absolute value of the reference thermometer.

8.5.2 Probe and Stack Thermocouple - For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice water, boiling water, and hot oil

bath temperatures must be performed. Use of a point at room air temperature is recommended. The thermometer and thermocouple must agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

8.6 Barometer - Adjust the barometer initially and before each test series to agree to within ±2.5 mm Hg (0.1 in. Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

8.7 Triple-beam or Electronic Balance - Calibrate the balance before each test series, using Class S standard weights. The weights must be within ±0.5% of the standards, or the balance must be adjusted to meet these limits.

9.0 CALCULATIONS

Perform calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

9.1 Total Formaldehyde - Determine the total formaldehyde in mg, using the following equation:

$$\text{Total mg formaldehyde} = C_d \times V \times DF \times \left[\frac{\text{g/mole aldehyde}}{\text{g/mole DNPH derivative}}\right] \times 10^{-3} \text{ mg/µg}$$

where:

C_d = measured concentration of DNPH-formaldehyde derivative, µg/mL
V = organic extract volume, mL
DF = dilution factor

9.2 Formaldehyde Concentration In Stack Gas - Determine the formaldehyde concentration in the stack gas using the following equation:

$$C_f = K \text{ [total formaldehyde, mg]} / V_{m(std)}$$

where:

K = 35.31 ft^3/m^3 if $V_{m(std)}$ is expressed in English units
= 1.00 m^3/m^3 if $V_{m(std)}$ is expressed in metric units
$V_{m(std)}$ = volume of gas sample as measured by dry gas meter, corrected to standard conditions, dscm (dscf)

9.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop are obtained from the data sheet.

9.4 Dry Gas Volume - Calculate $V_{m(std)}$ and adjust for leakage, if necessary, using the equation in Sec. 6 of Method 5.

9.5 Volume of Water Vapor and Moisture Content - Calculate the volume of water vapor and moisture content from Equations 5-2 and 5-3 of Method 5.

10.0 DETERMINATION OF VOLUME TO BE SAMPLED

To determine the minimum sample volume to be collected, use the following sequence of equations.

10.1 From prior analysis of the waste feed, the concentration of formaldehyde (FORM) introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the maximum amount of FORM allowed to be present in the effluent. This amount may be expressed as:

$$\text{Max FORM}_i \text{ Mass} = [(WF)(\text{FORM}_i \text{ conc})(100 - \%DRE)] / 100$$

where:

WF = mass flow rate of waste feed per h, g/h (lb/h)
FORM_i = concentration of FORM (wt %) introduced into the combustion process
DRE = percent Destruction and Removal Efficiency required
Max FORM = mass flow rate (g/h [lb/h]) of FORM emitted from the combustion sources

10.2 The average discharge concentration of the FORM in the effluent gas is determined by comparing the Max FORM with the volumetric flow rate being exhausted from the source. Volumetric flow rate data are available as a result of preliminary Method 1 - 4 determinations:

$$\text{Max FORM}_i \text{ conc} = [\text{Max FORM}_i \text{ Mass}] / DV_{eff(std)}$$

where:

$DV_{eff(std)}$ = volumetric flow rate of exhaust gas, dscm (dscf)
FORM_i conc = anticipated concentration of the FORM in the exhaust gas stream, g/dscm (lb/dscf)

10.3 In making this calculation, it is recommended that a safety margin of at least ten be included.

$$[LDL_{FORM} \times 10] / [\text{FORM}_i \text{ conc}] = V_{tbc}$$

where:

LDL_{FORM} = detectable amount of FORM in entire sampling train
V_{tbc} = minimum dry standard volume to be collected at dry-gas meter

10.4 The following analytical detection limits and DNPH Reagent Capacity (based on a total volume of 200 mL in two impingers) must also be considered in determining a volume to be sampled.

11.0 QUALITY CONTROL

11.1 Sampling - See EPA Manual 600/4-77-027b for Method 5 quality control.

11.2 Analysis - The quality assurance program required for this method includes the analysis of field and method blanks, procedure validations, analysis of field spikes, and analysis of reagent checks. The assessment of combustion data and positive identification and quantitation of formaldehyde are dependent on the integrity of the samples received and the precision and accuracy of the analytical methodology. Quality Assurance procedures for this method are designed to monitor the performance of the analytical methodology and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

11.2.1 Field Blanks - Field blanks may be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, methylene chloride and water, and unused DNPH reagent. In the case of results exceeding regulatory limits, field blank data may be useful for convincing the regulatory official that contamination was the cause. This may result in retesting rather than a violation charge. Collection of the field blank is optional but recommended.

11.2.2 Method Blanks - A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

11.2.3 Field Spikes - A field spike is performed by introducing 200 µL of the Field Spike Standard into an impinger containing 200 mL of DNPH solution. Standard impinger recovery procedures are followed and the field spike sample is returned to the laboratory for analysis. The field spike is used as a check on field handling and recovery procedures. An aliquot of the field spike standard is retained in the laboratory for derivatization and comparative analysis.

11.2.4 Matrix Spike Sample - In addition to those stack samples necessary for basic data needs, one complete sample (of the same time duration) must be collected for use as a matrix spike sample as described in Sec. 8.0 of Method 8315. This sample must be recovered and shipped in exactly the same manner as the other stack samples. Every effort should be made to ensure that this sample represents the average stack matrix of the sample batch. For example, the matrix spike sample should be taken the same day as the other samples in the group, if at all possible. If it is known or suspected that the stack gas matrix is varying widely during the overall sampling run, it is advisable to take more than one matrix spike sample and composite them.

11.2.5 DNPH Reagent Checks - An aliquot of the extracted DNPH reagent is prepared and analyzed according to the procedure in Sec. 5.4.3 to ensure that the background in the reagent is acceptable for field use.

12.0 METHOD PERFORMANCE

Method performance evaluation - The expected method performance parameters for precision, accuracy, and detection limits are provided in Table 3.

13.0 REFERENCES

1. 40 CFR Part 60, Appendix A, Test Methods.

2. Martin, R.M., "Construction Details of Isokinetic Source-Sampling Equipment", U.S. Environmental Protection Agency, Research Triangle Park, NC, Air Pollution Technical Document (APTD) 0581, April 1971.

3. Rom, J.J., "Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment", U.S. Environmental Protection Agency, Research Triangle Park, NC, Air Pollution Technical Document (APTD) 0576, March 1972.

4. Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials (ASTM), Philadelphia, PA, 1974, pp. 617-622.

TABLE 1

APPROXIMATE AMOUNT OF CRYSTALLINE DNPH USED
TO PREPARE A SATURATED SOLUTION

Amount of Moisture in DNPH	Weight Required per 8 L of Solution
10 weight percent	36 g
15 weight percent	38 g
30 weight percent	46 g

TABLE 2

OPTIMUM STACK DETECTION LIMITS[a] AND REAGENT SAMPLING CAPACITY[b] FOR FORMALDEHYDE ANALYSIS

Analyte	CAS No.	Detection Limit[a] (ppbv)	Reagent Capacity	
			ppmv	mg/m^3
Formaldehyde	50-00-0	36	7.5	9
Acetaldehyde	75-07-0	34	7.5	14
Acetone	67-64-1	30	7.5	17
Propionaldehyde	123-38-6	30	7.5	17
Butyraldehyde	123-72-8	30	7.5	21
Valeraldehyde	110-62-3	30	7.5	25
Isovaleraldehyde	590-86-3	28	7.5	25
Hexaldehyde	66-25-1	26	7.5	30
Benzaldehyde	100-52-7	28	7.5	33
Acetophenone	98-86-2	28	7.5	37
o-Tolualdehyde	529-20-4	26	7.5	37
m-Tolualdehyde	620-23-5	26	7.5	37
p-Tolualdehyde	104-87-0	26	7.5	37
2,5-Dimethylbenzaldehyde	5779-94-2	24	7.5	41
Isophorone	78-59-1	24	7.5	42

[a]Detection limits are determined based on 400 mL of reagent and 10 times the instrument detection limit using hydrazones in solvent, and therefore, represent the optimum capability of the method.

[b]Based on 400 mL of reagent, a reagent concentration of 10 mM DNPH, a 1.3 cubic meter sample size and a safety factor of 10.

TABLE 3

EXPECTED METHOD PERFORMANCE BASED ON DUAL TRAINS

Compound	Precision (%RPD)[1]	Accuracy (%)[2]	Detection Limit (ppbv)[3]
Formaldehyde	±21	±10	±90
Acetaldehyde	±17	±21	±40
Propionaldehyde	±49	±23	±60
Acetophenone	±44	±10	±10
Isophorone	±9	±8	±10

[1] Relative percent difference limit for dual trains.
[2] Limit for field spike recoveries.
[3] The lower reporting limit having less than 1% probability of false positive detection.

FIGURE 1
SAMPLING TRAIN FOR ALDEHYDES AND KETONES

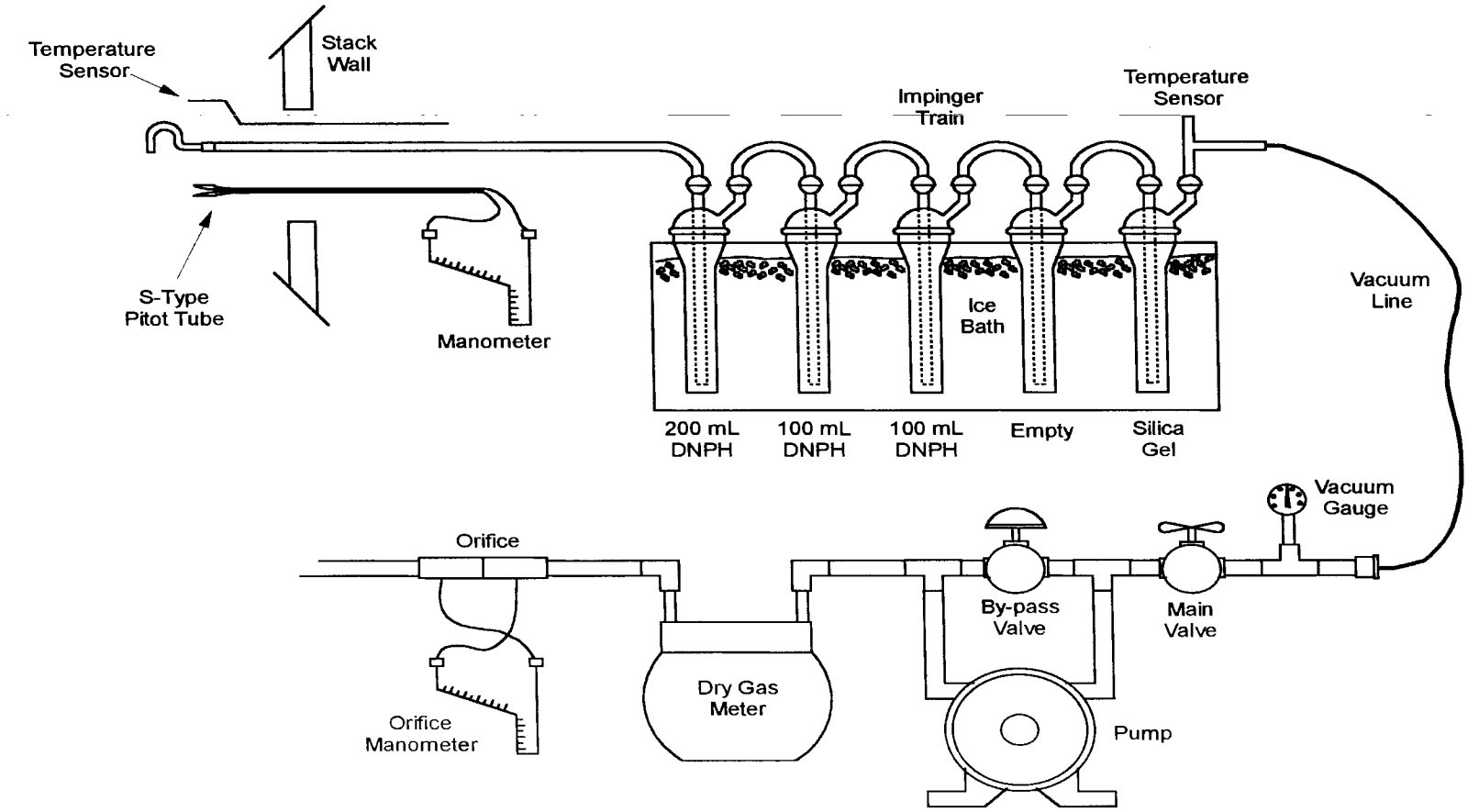


FIGURE 2
FIELD SAMPLING DATA FORM

Plant _____

Location _____

Operator _____

Date _____

Run Number _____

Sample Box No. _____

Meter Box No. _____

Meter H@ _____

C Factor _____

Pitot Tube Coefficient C_p _____

Schematic of Stack Cross Section

Ambient Temperature _____

Barometric Pressure _____

Assumed Moisture % _____

Probe Length _____ m (ft)

Nozzle Ident. No. _____

Average Calibrated Nozzle Diameter _____ cm (in)

Probe Heating Setting _____

Leak Rate _____ m^3/min (cfm)

Probe Liner Material _____

Static Pressure _____ mm Hg (in.Hg)

Filter No. _____

Traverse Point Number	Sampling Time (Min.)	Vacuum mm Hg (in. Hg)	Stack Temperature (T_s) °C (°F)	Velocity head (ΔP) mm (in) H_20	Pressure Differential Across Orifice Meter mm (H_20) (in. H_20)	Gas Sample Volume m^3 (ft^3)	Gas Sample Temp. at Dry Gas Meter		Filter Holder Temp. °C (°F)	Temp. of Gas Leaving Last Impinger °C (°F)
							Inlet °C (°F)	Outlet °C (°F)		
Total							Avg	Ave		
Average										

APPENDIX A

ADDITION OF A FILTER TO THE FORMALDEHYDE SAMPLING TRAIN

As a check on the survival of particulate material through the impinger system, a filter can be added to the impinger train either after the second impinger or after the third impinger. Since the impingers are in an ice bath, there is no reason to heat the filter at this point.

Any suitable medium (e.g., paper, organic membrane) may be used for the filter if the material conforms to the following specifications:

1) The filter has at least 95% collection efficiency (<5% penetration) for 3 µm dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose.

2) The filter has a low aldehyde blank value (<0.015 mg formaldehyde/cm^2 of filter area). Before the test series, determine the average formaldehyde blank value of at least three filters (from the lot to be used for sampling) using the applicable analytical procedures.

Recover the exposed filter into a separate clean container and return the container over ice to the laboratory for analysis. If the filter is being analyzed for formaldehyde, the filter may be recovered into a container or DNPH reagent for shipment back to the laboratory. If the filter is being examined for the presence of particulate material, the filter may be recovered into a clean dry container and returned to the laboratory.

METHOD 0020

SOURCE ASSESSMENT SAMPLING SYSTEM (SASS)

1.0 PRINCIPLE AND APPLICATION

1.1 Principle

1.1.1 Particulate and semivolatile organic materials are withdrawn from a source at a constant rate near isokinetic conditions and are collected in a multicomponent sampling train.

1.1.2 Three heated cyclones and a heated high-efficiency fiber filter remove and collect the particulate material from the sample and a packed bed of porous polymeric resin adsorbs the condensible organic vapors.

1.1.3 Chemical analyses of the sample are conducted to determine the concentration and identity of the semivolatile organic species and gravimetric determinations are performed to approximate particulate emissions.

1.2 Application: This method is applicable to the preparation of semiquantitative estimates (within a factor of three) of the amounts and types of semivolatile organic and particulate materials that are discharged from incineration systems.

2.0 APPARATUS

2.1 Sampling Train: A schematic of the sampling train used in this method is given in Figure 1. This sampling train configuration is that of the Source Assessment Sampling System (SASS), as supplied by the manufacturer. Basic operating and maintenance procedures are described in the "Operating and Service Manual: Source Assessment Sampling System" supplied on purchase of the sampling system (Blake, 1977). Users should refer to this document and adopt, but not limit themselves to, its operating and maintenance procedures. The SASS train components and specifications are detailed below.

2.1.1 **Probe nozzles:** The probe nozzles are constructed of Type 316 seamless stainless steel tubing and have sharp leading edges. The nozzles are a hybrid elbow/buttonhook design, obtainable in diameters ranging from 0.31 to 1.91 cm (1/8 to 3/4 in.), and are interchangeable. Each nozzle should be calibrated according to the procedure outlined in Paragraph 7.2 of this method.

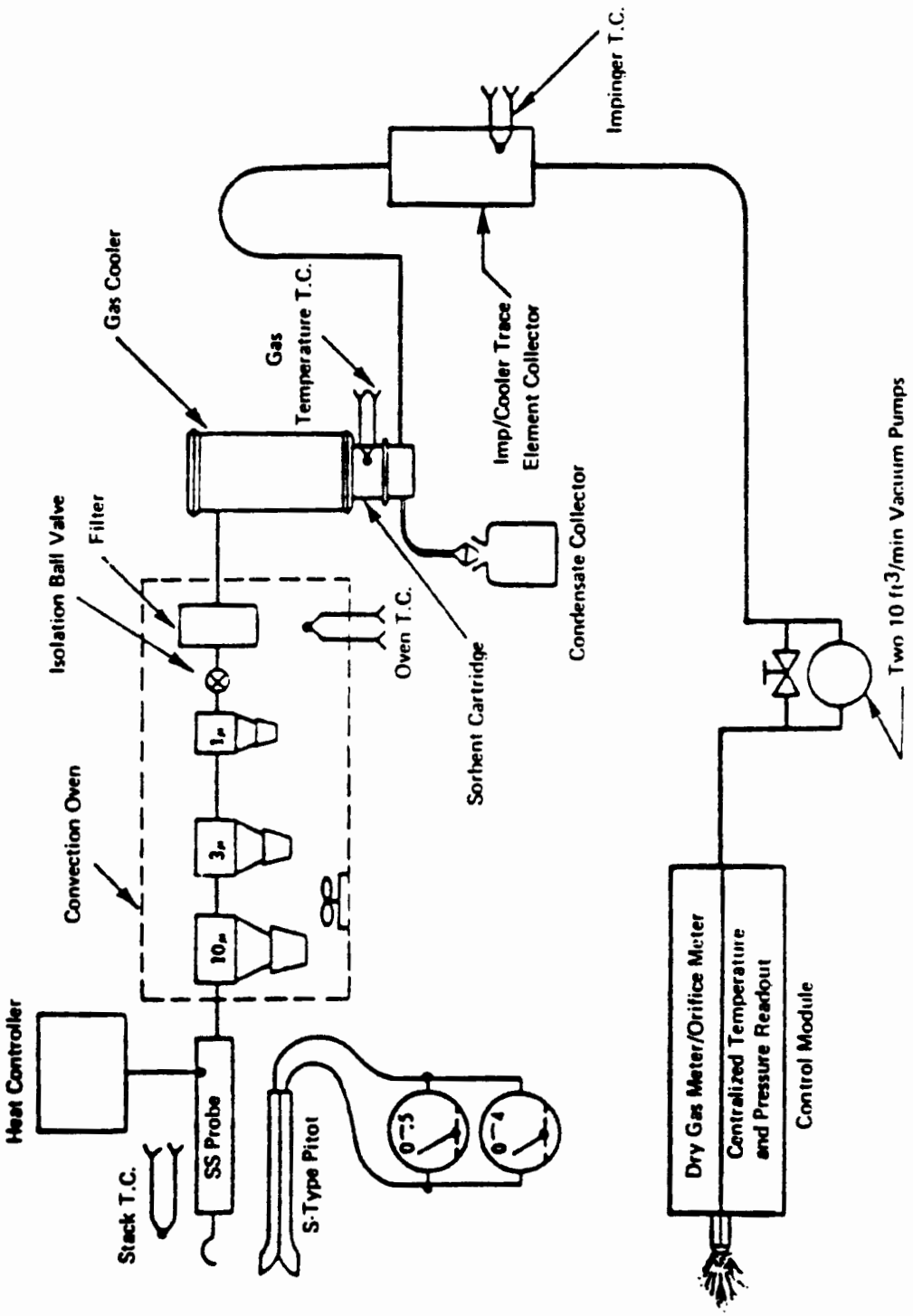


Figure 1. SASS Schematic Diagram.

2.1.2 **Probe Liner:**

2.1.2.1 The probe liner is also constructed of Type 316 seamless stainless steel tubing; attached to the liner is a proportional temperature controller capable of maintaining the liner surface temperature at 204 $\pm$ 20°C (400 $\pm$ 36°F) during sampling. The use of the proportional controller to control the liner surface temperature at the control module is preferred because the oven often cannot be reached for adjustment during sampling.

2.1.2.2 It should be noted that the measurement of the probe liner surface temperature is not an accurate measurement of the internal gas stream temperature, which is the temperature of interest. This source of error is caused by the temperature gradient that exists between the inner and outer walls of the liner. Monitoring of the actual gas stream temperature is impractical with the SASS trains as presently constructed. It is suggested that a one-time calibration be conducted in which the internal gas stream temperature is compared to the liner surface at various temperatures and at the standard SASS flow rate of 4.0 scfm.

2.1.2.3 The probe and probe liner can withstand points up to 370°C (700°F), at which temperature they will soften. However, stack temperatures greater than 288°C (550°F) may result in gas temperatures at the 10-um cyclone inlet greater than the recommended 204°C (400°F) and hence require the use of a special water- or forced-air-cooled probe.

2.1.3 **Pitot tubes:** The pitot tubes are Type S, designed to meet the specifications of EPA Method 2 (see Reference below); these are attached to the probe sheath to allow constant monitoring of the stack gas velocity. The point of attachment to the sheath is such that the impact (high pressure) opening plane of the pitots is level with or above the sampling nozzle entry plane, as required by Method 2, to eliminate nozzle interference in velocity measurements. If calibration is not required, the pitot tubes are assigned a nominal coefficient of 0.84, as described in the calibration section of this method.

2.1.4 **Differential pressure gauges:** Three Magnehelic-type gauges are used. One gauge (0 to 0.5 in. H_2O) monitors the pressure drop across the orifice meter (ΔH_i); the other two gauges (0 to 0.5 and 0 to 4.0 in. H_2O) are connected in parallel and indicate the pressure differential across the pitot tubes used for measuring stack gas velocity.

2.1.5 **Filter holder and filter support:** The filter holder and filter support screen are constructed of Type 316 stainless steel with a

Teflon gasket providing an airtight seal around the circumference. The holder is attached immediately to the outlet of the 1-um cyclone or the cyclone bypass.

2.1.6 **Cyclone/Filter heating system:** The cyclone/filter heating system is an insulated double-walled oven, capable of maintaining the temperature in the area of the cyclones and filter holder around the recommended 204°C (400°F). A chromel-alumel thermocouple for temperature sensing allows feedback control of the temperature to within approximately 10%.

2.1.7 **Cyclone train:** The cyclone train consists of three cyclone separators in series, having nominal particle-size cutoff diameters of 10, 3, and 1 um respectively. The material of construction is Type 316 stainless steel with Teflon gaskets sealing the hoods and collector cups. The compact design of the 10-um cyclone is achieved by incorporating flow-interrupting vanes in the collection cup.

2.1.8 **Organic module:** The organic module consists of a thin-film heat exchanger/gas cooler, a sorbent cartridge, and a condensate collection trap. The temperature of the heat exchanger fluid is regulated by activating an immersion heater or routing the coolant through another heat exchanger in the impinger ice water bath. Water from the impinger bath is continually circulated through the inner reservoir of the gas cooler for additional cooling capacity. The sorbent cartridge encloses the polymeric adsorbent bed in a cylinder covered on both ends by 80-mesh, Type 316 stainless steel wire cloth. The cartridge holds approximately 150 grams of XAD-2 adsorbent resin. Condensed moisture from the gas stream is collected in a reservoir located directly beneath the packed sorbent bed. The drain valve of the reservoir should be coupled with a Teflon line to an appropriately sized (1- to 5-liter) glass storage container, as the capacity of the reservoir will typically be exceeded during a run.

2.1.9 **Impinger train:** The four impingers have a capacity of approximately 3 liters each and are constructed of pyrex glass. The caps are Teflon with stainless steel fittings and the impingers are interconnected by flexible Teflon or stainless steel tubing. The first two impingers are equipped with splash guards to minimize fluid carryover and the last impinger with a thermocouple mounted in the cap for monitoring the impinger train exit gas temperature.

2.1.10 **Pump/Metering system:** Two leak-free vane-type vacuum pumps connected in parallel are used to maintain the 4.0-scfm flow in the sampling system. Vacuum and differential pressure gauges, thermocouples capable of measuring temperature to within 3°C (5.4°F) and a dry gas meter capable of measuring volume to within 2% are supplied as the other necessary components for maintaining isokinetic sampling rates.

2.1.11 **Barometer:** An aneroid barometer, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.5 in. Hg), is required, unless the barometric reading is obtained from a nearby National Weather Station; the station value (i.e., the absolute barometric pressure) must be corrected for elevation differences between the weather station and the sampling point. The corrected value should reflect a decrease of 2.5 mm Hg (0.1 in. Hg) per 30-m (100-ft) elevation increase, and vice versa for elevation decrease. (See Paragraph 7.7).

2.1.12 **Gas density determination apparatus:** The length of a SASS run is typically sufficient to determine the average gas stream density during the run. EPA Method 3 should be consulted for detailed specifications for an integrated fixed gas sampling system. Analysis of the collected samples should be performed with an ORSAT analyzer or a GC/TCD system outfitted specifically for this purpose.

2.1.13 **Calibration/Field preparation log:** For documentation of calibration and preparation procedures, a permanently bound laboratory notebook is recommended, in which carbon copies are made of the data as they are being recorded. The carbon copies should be detachable and used only for separate storage in the test program archives.

2.2 Sample recovery:

2.2.1 **Probe liner brush:** The brush must have nylon bristles, a stainless steel wire handle, and extensions of stainless steel, Teflon, or other inert material. The combined extensions must be equal to or greater than the length of the probe.

2.2.2 **Probe nozzle brush:** The brush must have nylon bristles and a stainless steel wire handle, and be properly sized and shaped for cleaning the inner surfaces of the nozzle.

2.2.3 **Cyclone and filter holder brushes:** The brushes must have nylon bristles and a stainless steel wire handle, and be properly sized for cleaning the inner walls of these components. It is strongly recommended that a separate brush be used for sample recovery from each of these components to avoid cross contamination of one particle size fraction by another.

2.2.4 **Wash bottles:** Three are needed. Teflon or glass is required to avoid contamination of organic solvents; Teflon is preferred because it is unbreakable.

2.2.5 **Glass sample storage containers:** The containers must be chemically resistant, borosilicate glass bottles, 500-mL or 1,000-mL. Screw-cap liners should be Teflon or constructed so as to be leak-free and resistant to chemical attack by organic recovery solvents (narrow-mouth glass bottles have been found to exhibit less tendency toward leakage).

2.2.6 **Petri dishes:** These must be glass and sealed around the circumference with Teflon tape for storage and transport of filter samples.

2.2.7 **Graduated cylinder and triple-beam balance:** to measure condensed water to the nearest 1 mL or 0.5 g. Graduated cylinders must have subdivisions no greater than 2 mL. Equipment made of glass must be used for measuring the volume of any solution that will be subject to organic analysis. Laboratory triple-beam balances must be capable of weighing to ±0.5 g or better.

2.2.8 **High-density linear polyethylene (HDLP) storage containers:** These are used for storage of the impingers.

2.2.9 **Plastic storage containers:** Airtight containers are necessary for storage of silica gel.

2.2.10 **Funnels:** Glass funnels must be used in recovering samples for organic analysis. Glass or plastic funnels may be used in other processes but care must be taken to segregate the two types.

3.0 REAGENTS AND MATERIALS

3.1 Filters: Glass fiber filters, 15.24 cm (6.0 in.) in diameter without organic binder, exhibiting 99.95% efficiency (<0.05% penetration) on 0.3-micron dioctyl phthalate smoke particles, conforming to the specifications outlined in ASTM Standard Method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose. The filter material must also be unreactive to SO_2 and SO_3.

3.2 Adsorbent resin: Porous polymeric resin, XAD-2, is used. The resin must be cleaned prior to use. The resin must not exhibit a blank higher than 4 mg/kg of total chromatographable organics (TCO) prior to use. Once cleaned, the resin should be stored in a wide-mouth amber glass container and the headspace purged with nitrogen to limit exposure to ambient air. Resin should be used within 2 wk of preparation.

3.3 Silica gel: Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hr. New silica gel may be used as received.

3.4 Impinger solutions: Since the impinger solutions are typically used for the determination of gas-stream water-vapor content, Type II water should be used. If specific inorganic species are to be determined (e.g., hydrochloric acid when burning chlorinated organic material), then other appropriate collecting solutions (in the above example, dilute base) must be used.

3.5 Crushed ice: Commercially available. Quantities ranging from 50 to 100 lb may be necessary during a run, depending upon ambient air temperatures.

3.6 Methanol/Methylene chloride: Distilled-in-glass or pesticide-grade methanol and methylene chloride are required.

4.0 SAMPLING PROCEDURE

4.1 Sampling equipment calibration:

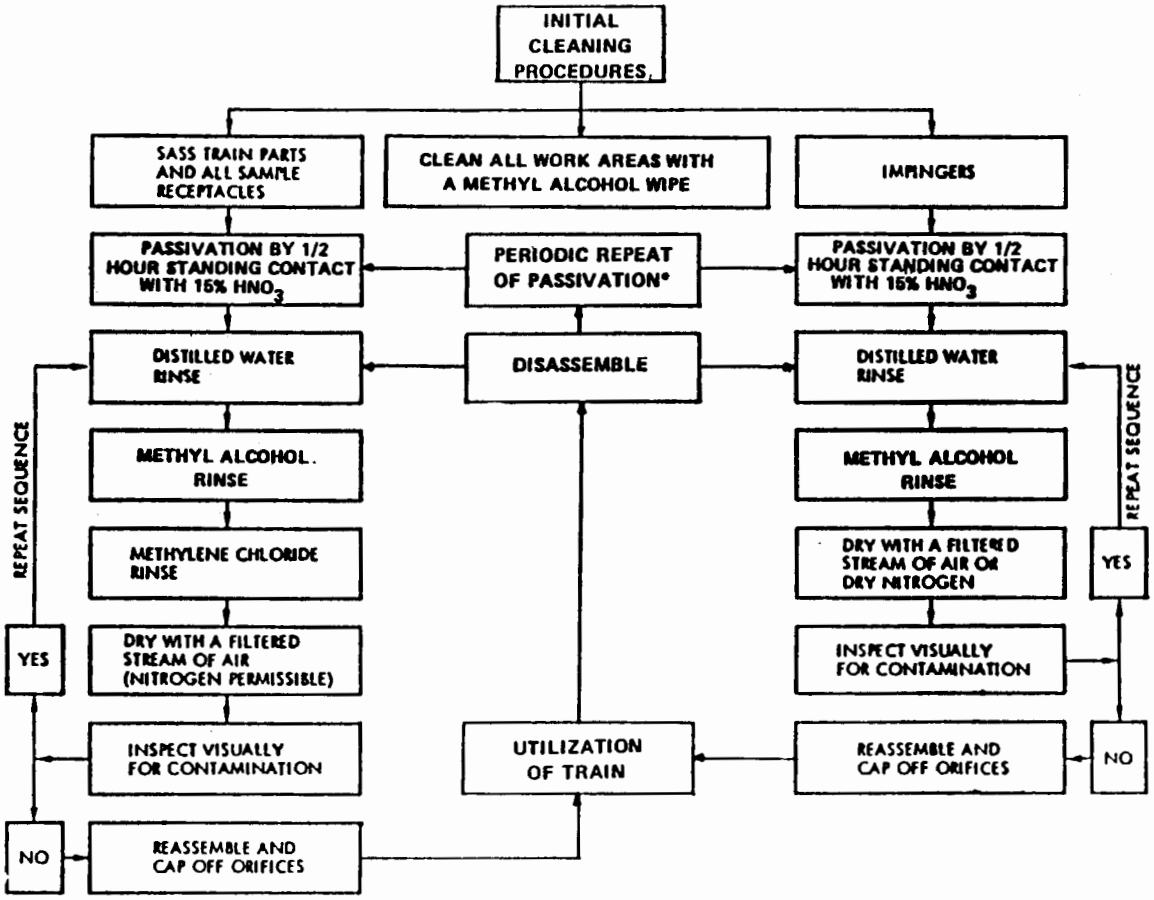
4.1.1 The probe tips, pitot tubes, dry gas meter, thermocouples, and any thermometers must be calibrated before and after each field sampling trip according to the procedures outlined in APTD-0576 (Rom, 1972) and below in Section 7.0. During extended sampling trips where the train will routinely be used more than 10 times, it is strongly recommended that a calibrated orifice, a set of micrometers (Vernier calipers), and a standard mercury-in-glass thermometer accompany the train to verify that the calibrations of the dry gas meter, probe nozzles, and thermocouples, respectively, have not changed significantly (more than ±2%). The aneroid barometer should be calibrated on a daily basis against a mercury barometer when in the laboratory and periodically in the field by consulting the local weather station and correcting for elevation (see Paragraph 7.7).

4.2 Laboratory preparation:

4.2.1 Weigh several 700- to 800-g portions of silica gel in airtight containers to ±0.1 g. Record the weight of the silica gel plus the container on the container and in a field sampling preparation notebook.

4.2.2 Holding with blunt-tipped tweezers, check filters visually against light for irregularities, flaws, or pinhole leaks. Label the shipping containers (glass Petri dishes) and keep the filters in these containers at all times except during sampling and weighing. The filters themselves need not be labeled if strict compliance with the above instruction is ensured. Desiccate the filters in a desiccator over Drierite or silica gel with the Petri dishes open at 20 ± 5.6°C (68 + 10°F) and ambient pressure for at least 24 hr and weigh. Thereafter weigh at 6-hr (minimum) intervals to a constant weight, i.e., previous weight ±0.5 mg; record the weight to the nearest 0.1 mg, along with the date and time, in the field sampling preparation notebook. Alternatively, the filters may be oven-dried at 105°C (220°F) for 2 to 3 hr, desiccated for 2 hr, weighed, and weighed thereafter at 6-hr intervals to a constant weight. During each weighing, the filter must not be exposed to the laboratory atmosphere for longer than 2 min with a relative humidity greater than 50%.

4.2.3 Passivate all SASS train parts and sample storage containers, referring to the procedure that appears in Figure 2, adapted from Level I requirements. Passivation is required of all new train components and sample storage containers before their initial use in the field. Thereafter, passivation should be conducted every 6 months when the frequency of tests is once per month or less, and every 3 months when the



SASS Cleaning Procedures
Source: "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Ed.) EPA-600/7-78-201

Figure 2. SASS Cleaning Procedure

frequency is between once per week and once per month. If testing is more frequent, passivation should be conducted proportionately more often. Whenever corrosion has occurred, the corrosion must be removed and the passivation repeated. The passivation and rinse solutions should be replaced every fourth use, or discarded weekly.

4.2.4 Prepare recycled sample containers by detergent washing (using a stiff nylon brush where necessary), followed by rinsing with Type II water, methanol and methylene chloride. As each part is treated with the final solvent, dry with filtered air or dry nitrogen and inspect for any contaminating residue. Discard any container exhibiting visual contamination. Cover all open surfaces with aluminum foil or Teflon film, using elastic bands to secure.

4.2.5 Assembly and leak-checking of the entire train in the laboratory is highly recommended to reveal the need for replacement of gaskets or defective components. The leak-check procedure is described in Paragraph 4.4.3.11. Substitution of Viton-A gaskets for Teflon may facilitate meeting the allowable leak rate. A length of Teflon tape stretched around the circumference of each flanged connection underneath the ring clamp also greatly reduces inward air leakage.

4.3 Preliminary field determinations:

4.3.1 Select the sampling site and remove any accumulated scale and corrosion from the sampling portholes. Determine the stack static pressure, temperature, and velocity profile using EPA Method 2 (see References); a leak-check of the pitot lines prior to conducting these measurements is highly recommended. Approximate the moisture content using EPA Method 4 (Approximation Method) or alternate means such as drying tubes, wet bulb/dry bulb or condensation techniques, stoichiometric calculations, or previous experience. Determine the dry molecular weight of the stack gas by performing an ORSAT or GC/TCD analysis for CO, CO_2, O_2 and N_2 on an average of three grab samples taken from either the center of the duct or a point no closer to the stack walls than **1.0 m (3.3 ft).**

4.3.2 Select a nozzle size based upon the calculations below, ensuring that it will not be necessary to change the nozzle during the sampling run to maintain near-isokinetic sampling rates.

4.3.2.1 To calculate the required nozzle diameter, first calculate the Average Stack Gas Velocity:

$$(V_s)_{avg} = K_p C_p (\sqrt{(\Delta P)})_{avg} \left[\sqrt{\frac{(T_s)_{avg}}{P_s M_s}} \right]$$

where:

$(V_s)_{avg}$ = Average stack gas velocity, ft/sec;

$$K_p = 85.48 \left[\frac{\text{ft}}{\text{sec}} \left[\frac{(\text{lb/lb-mole})(\text{in. Hg})}{^\circ\text{R}(\text{in. } H_2O)} \right]^{1/2} \right];$$

C_p = Pitot tube coefficient, dimensionless;

ΔP = Velocity head of stack gas, in. H_2O;

$(T_s)_{avg}$ = Average stack gas temperature, °R;

P_s = Absolute stack gas pressure, in. Hg; and

M_s = Molecular weight of stack gas (wet basis), lb/lb-mole.

4.3.2.2 Then calculate the required Nozzle Diameter (D_n):

$$D_n = 0.831 \left[\frac{(T_s)_{avg}}{(V_s)_{avg} P_s} \right]$$

4.3.3 Select a suitable probe length such that one or more points of average velocity can be sampled. Determine the total length of sampling time by comparing the anticipated average sampling rate to the volume requirement of 30 dscm (approximately 1,060 dscf).

4.3.3.1 The anticipated Average Sampling Rate is calculated as follows:

$$Q_{mo} = (1-B_{ws})Q_{st} \frac{P_{st} (T_m)_{avg}}{P_m (T_{st})}$$

where:

Q_{mo} = Flow rate through orifice at meter conditions, ft^3/min (dry);

B_{ws} = Volume fraction of water vapor in the gas stream, dimensionless;

Q_{st} = Design sampling flowrate for SASS train, 4.0 scfm;

P_{st} = Standard presssure, 29.92 in. Hg;

$(T_m)_{avg}$ = Average gas temperature (estimated) at the dry gas meter, °R;

P_m = Absolute meter pressure, in. Hg, calculated by

$$P_m = P_b + \frac{(\Delta H)_{est.avg.}}{13.6}$$

where:

$(\Delta H)_{est.avg.}$ = Estimated average ΔH across orifice, 3-4 in. H_2O, and

P_b = Barometric pressure (corrected), in. Hg; and

T_{st} = Standard temperature, 528°R.

None of these definitions has an English/metric equivalent.

4.3.3.2 Using this result, obtain the approximate sampling time by dividing the required sample volume by the estimated sampling flowrate.

4.3.4 Finally, calculate the Orifice Pressure Drop needed to maintain near-isokinetic sampling conditions from the equation:

$$\Delta H_i = \frac{P_m}{(T_m)_{avg}} \left[\frac{0.1924\ Q_{mo}}{J_i D_{oi}^2}\right]^2$$

where:

ΔH_i = Required ΔH across the orifice, in. H_2O;

P_m = Absolute meter pressure, in. Hg (calculated the same way as for Average Sampling Rate above);

$(T_m)_{avg}$ = Estimated average gas temperature at the dry gas meter, °R;

J_i = Orifice coefficient for orifice "i" (see Blake, 1977, and Section 7.0 of this method for determining orifice coefficients); and

D_{oi} = Orifice diameter, in. (information supplied upon purchase of the SASS train; the largest diameter orifice is typically best suited for the SASS sampling rate of 4.0 scfm).

4.3.5 It is desirable, but not required, to sample more than one point of average velocity during a SASS run. Allocate equal intervals of the total sampling time estimated above to each sampling point chosen if more than one point will be sampled.

4.4 Preparation of collection train:

4.4.1 An integral part of preparing the collection train is securing sufficient electrical power to operate for an extended period of time without interruption. Three separate circuits -- two 30-amp and one 20-amp -- are required. It is highly recommended that one sampling pump and one control box power cord (probe heater) be placed on one of the 30-amp circuits, and the other sampling pump and control box power cord (oven heater and temperature readout) be placed on the other 30-amp circuit. The organic module coolant pump and temperature controller should be placed on the smaller 20-amp circuit.

4.4.2 During assembly of the train, keep the inner surfaces of each component covered until it is integrated into the system and sampling is about to begin. Fill the sorbent trap section of the organic module with approximately 150 g of clean adsorbent XAD-2 resin. To avoid contamination, the trap should be placed upon a clean surface (i.e., aluminum foil rinsed with methylene chloride and air-dried) while filling; gloves should be worn. Pack the trap uniformly to eliminate potential channeling. Place 500 mL of Type II water or other appropriate solution into the first and second impingers, leave the third impinger empty, and place a preweighed portion of silica gel into the fourth.

NOTE: The choice of impinger solutions depends upon whether these will be used to collect selected inorganic species or simply to condense water vapor from the gas stream to measure percent moisture. For example, in an incinerator combusting chlorinated organic material, a solution of dilute base would typically be used to collect hydrochloride acid emissions.

Using blunt-tipped tweezers, place a tared filter into the filter holder. Ensure that the filter is centered and the gasket properly placed to prevent the gas stream from circumventing the filter. On the probe, mark the locations of the chosen sampling points with heat-resistant tape or paint.

4.4.3 The stepwise procedure for assembly of the train follows:

4.4.3.1 Place the oven on a table or rollers that will be used as a support throughout the run.

4.4.3.2 Assemble the three cyclones, using the vortex breaker supplied with the cyclone in the 10-um cyclone only. (To minimize leaks throughout the system, a strip of Teflon tape should be stretched around the circumference of each flanged seal and the ring clamp placed over and secured.) Do not use the vortex breakers supplied with the 3- and 1-um cyclones in the 3- and 1-um cyclones. Actual calibration data has shown that the use of the vortex breakers in the two smaller cyclones may result in unreproducible particle-size cutoff diameters (the particle size at which 50% collection efficiency is exhibited).

4.4.3.3 Attach the filter holder to the outlet of the 1-um cyclone and place the cyclones and filter holder together in the oven. Preheat a spare filter holder containing a tared filter on the oven floor; cover the holder openings with aluminum foil.

4.4.3.4 Attach the probe to the oven and to the 10-um cyclone.

4.4.3.5 Place the impingers in the tray in the impinger case and make the apropriate interconnections.

4.4.3.6 Connect the organic module inlet to the filter housing outlet and the organic module outlet to the first impinger inlet.

4.4.3.7 Connect the vacuum pumps in parallel to the fourth impinger outlet.

4.4.3.8 Connect all temperature sensors and power lines to the control unit. Check temperature indicators and controllers at ambient temperature.

4.4.3.9 Activate gas cooling system. Begin monitoring the XAD-2 temperature. Always check coolant level before supplying power. Ensure proper gas cooling system temperature before proceeding.

NOTE: IT IS EXTREMELY IMPORTANT THAT THE XAD-2 RESIN TEMPERATURE NEVER EXCEED 50°C, AS DECOMPOSITION WILL OCCUR. DURING TESTING, THE XAD-2 TEMPERATURE MUST NOT EXCEED 20°C FOR EFFICIENT CAPTURE OF THE SEMIVOLATILE ORGANIC SPECIES OF INTEREST.

4.4.3.10 Heat oven and probe to 204°C (400°F).

4.4.3.11 Run gas flow leak-check. The following instructions will facilitate the leak-checking procedure:

a. Open the isolation ball valve and plug the inlet to the probe with a rubber stopper or appropriate airtight cap.

b. Start the pumping system with the bypass valves fully open and the coarse valves completely closed. Partially open the coarse valves and slowly close the bypass valves until a vacuum of 127 mm Hg (5 in. Hg) is reached. Do not reverse the direction of the bypass valves as backflushing of the impinger solutions into the organic module will result. If the desired vacuum is exceeded, either leak-check at the higher vacuum or terminate the leak-check and begin again. Allow the system to equilibrate and measure the leakage rate. The allowable leak rate for the SASS train is 0.0014 m^3/min (0.05 ft^3/min) at this vacuum. Close the isolation ball valve and evacuate the train to 281 mm Hg (15 in. Hg). The leak rate through the back half of the train should be less than 0.0014 m^3/min (0.05 ft^3/min) at this vacuum.

c. When the leak-check is complete, slowly remove the plug from the probe tip and then slowly open the isolation ball valve.

d. When the vacuum drops to 127 mm Hg (5 in. Hg) or less, immediately close both coarse control valves together. Switch off the pumping system and reopen the bypass valves. The bypass valves should not be opened until the coarse valves have been closed.

4.4.4 Only post-test leak-checks are mandatory; however, experience has shown that pre-test leak-checks and leak-checks following component changes are necessary to ensure that invaluable sampling time is not lost as a result of an oversight or defective component.

4.5 Sample Collection: Constant monitoring of train operations before, during, and after the particulate run is essential in maintaining sample integrity. Listed below are sample collection guidelines:

4.5.1 With the coarse valves closed and bypass valves open, turn on the vacuum pumps and allow them to warm up. As the probe and oven are heating, prepare a SASS run data sheet as shown in 40 CFR Appendix A (see References below). Barometric pressure data should be recorded at least at the beginning and end of the run; once per hour is preferred.

4.5.2 When operating temperatures have been reached, place the probe in the stack at the first designated sampling point, turn on the vacuum pumps, adjust the sampling flowrate to achieve the calculated ΔHi, and start the elapsed timer. If, however, the gas stream is under medium or high negative pressure, it becomes extremely important to start the vacuum pumps just before placing the probe in the gas stream, and to continue to operate the pumps until just after the probe has been removed from the gas stream. This will eliminate the possibility of lifting of the filter or backflushing of the filter and cyclone particulate catches at any time.

4.5.3 Seal the sampling port around the probe to prevent introduction of dilution air at this point. Record the clock time of the start of the test.

4.5.4 Using the criteria outlined above under Paragraph 4.3, Preliminary Field Determination, place the integrated fixed gas bag or bulb sampling probe into the gas stream and begin sampling. Collect three samples during the SASS run; record the initial and final clock times of each integrated fixed gas sample.

4.5.5 Monitor and maintain all temperatures and the calculated ΔH and record the data at equal intervals of 10-15 min.

4.5.6 Add crushed ice to the impinger section and drain excess water as necessary.

4.5.7 Without interrupting sampling, drain the condensate initially every 30-45 min, and afterward as necessary. Ensure that the vessel into which the reservoir is drained forms an airtight system with the reservoir using a connecting Teflon line, and is placed well below the level of the reservoir itself. To drain the reservoir, close the solation ball valve and open the drain valve. Allow the system to evacuate for 10-20 sec. Carefully open the isolation valve. The condensate should siphon from the reservoir into the storage vessel. Close the drain valve when the siphoning action of the condensate ceases.

4.5.8 Replace the filter when it becomes impossible to maintain near-isokinetic sampling rates but not more frequently than every 20 to 30 min. Always terminate and initiate sampling by adjustment of the coarse pump valves and then the bypass valves. A spare filter holder and filter, if available, should be preheating in the oven at all times. Conduct leak-checks before and after changing the filter. Recall previous instructions concerning removal and reintroduction of the probe into the duct.

4.5.9 At the same time, check the 1-um cyclone reservoir for remaining capacity, taking care not to contaminate the contents during this inspection.

4.5.10 When replacing a filter, start and stop the fixed gas sampling concurrently with the SASS sampling; record the clock time and dry-gas-meter reading whenever sampling is interrupted.

4.5.11 Upon collection of the required 30 dscm (1,060 dscf), remove the probe from the gas stream and shut down the pumps as previously instructed. Record the final dry-gas-meter reading and clock time; turn off all heaters. Conduct the post-test leak-check when the probe tip can be safely handled. Do not cap the probe while initially cooling, because this will create a vacuum inside that will cause disruption of the cyclone and filter particulate catches when it is released. Instead, use aluminum foil to cover probe openings. Before the probe is transported, secure the aluminum foil covers with elastic bands. Leak-check the pitot lines per EPA Method 2 to validate velocity heat data.

5.0 SAMPLE RECOVERY

The sample handling and transfer procedures outlined in this section have been adopted from the Level 1 procedures. The flow diagrammatic representation of the sample recovery procedures shown in Figures 3, 4, and 5 can be found in the Level 1 Sampling and Analysis Procedures Manual.

5.1 Disassembly of the SASS Train: At the conclusion of the sampling run, the train is disassembled and transported to the prepared work area as follows:

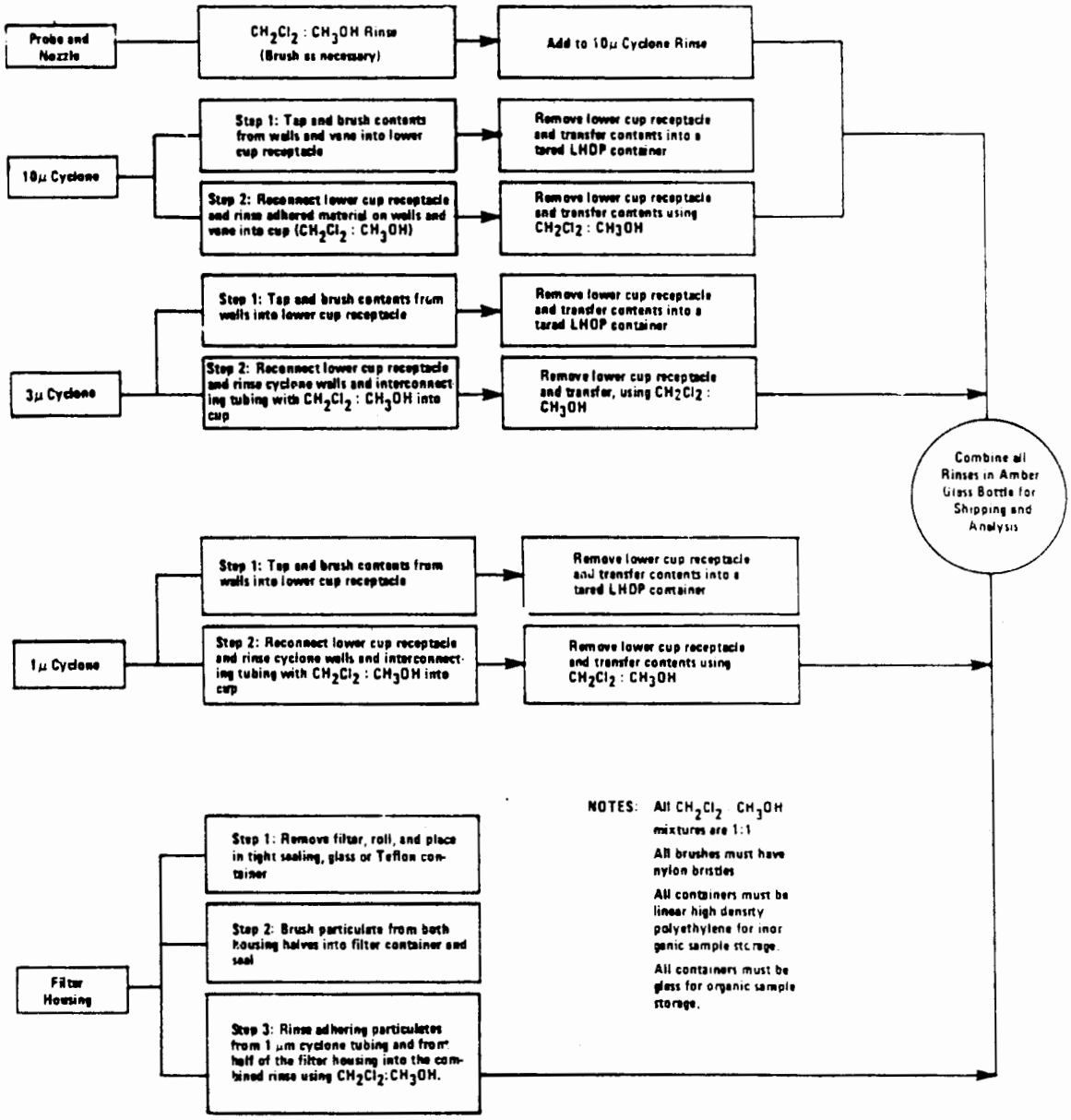


Figure 3. Sample Handling and Transfer Nozzle, Probe, Cyclones and Filter.

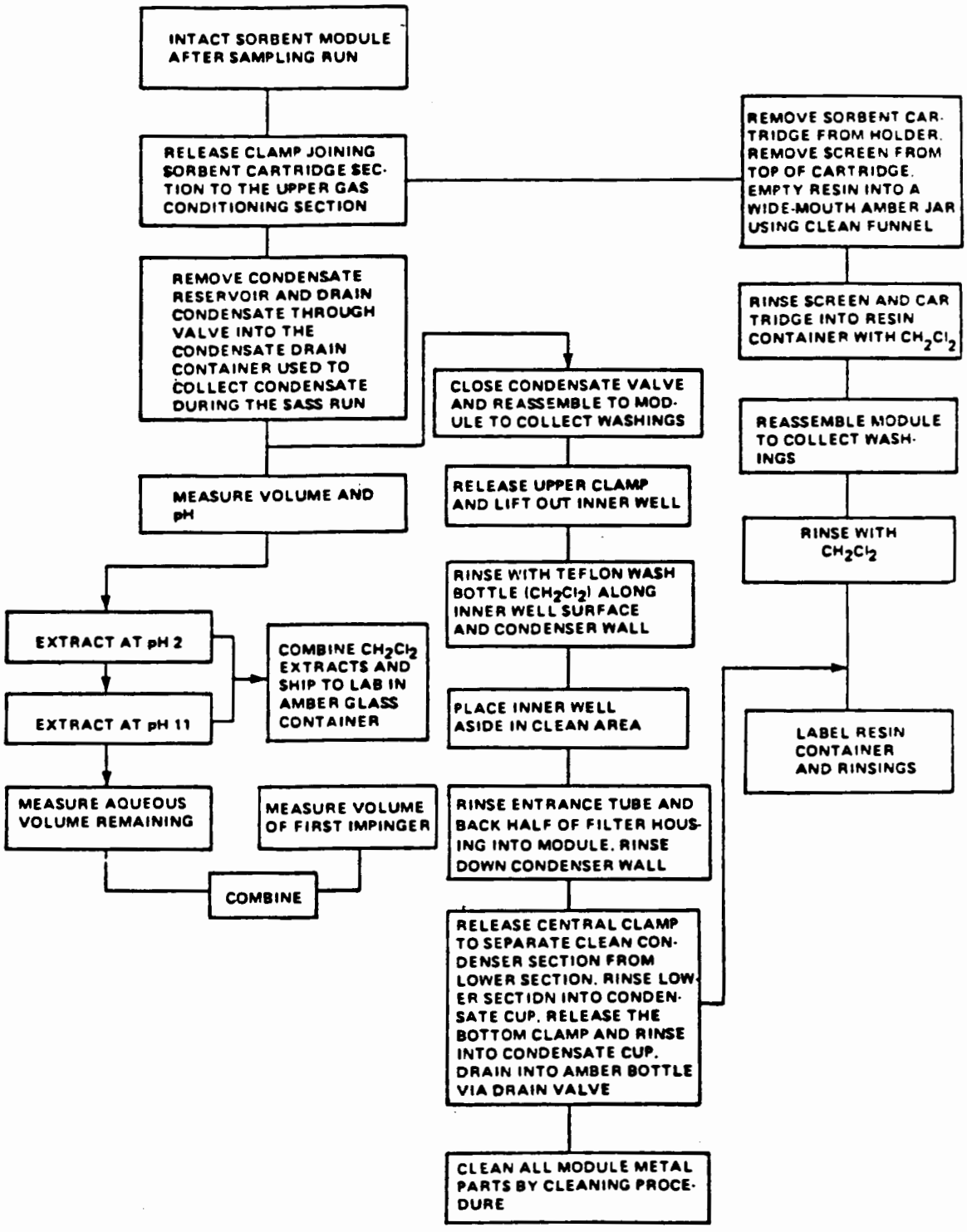


Figure 4. Sample Handling and Transfer XAD-2 Module.

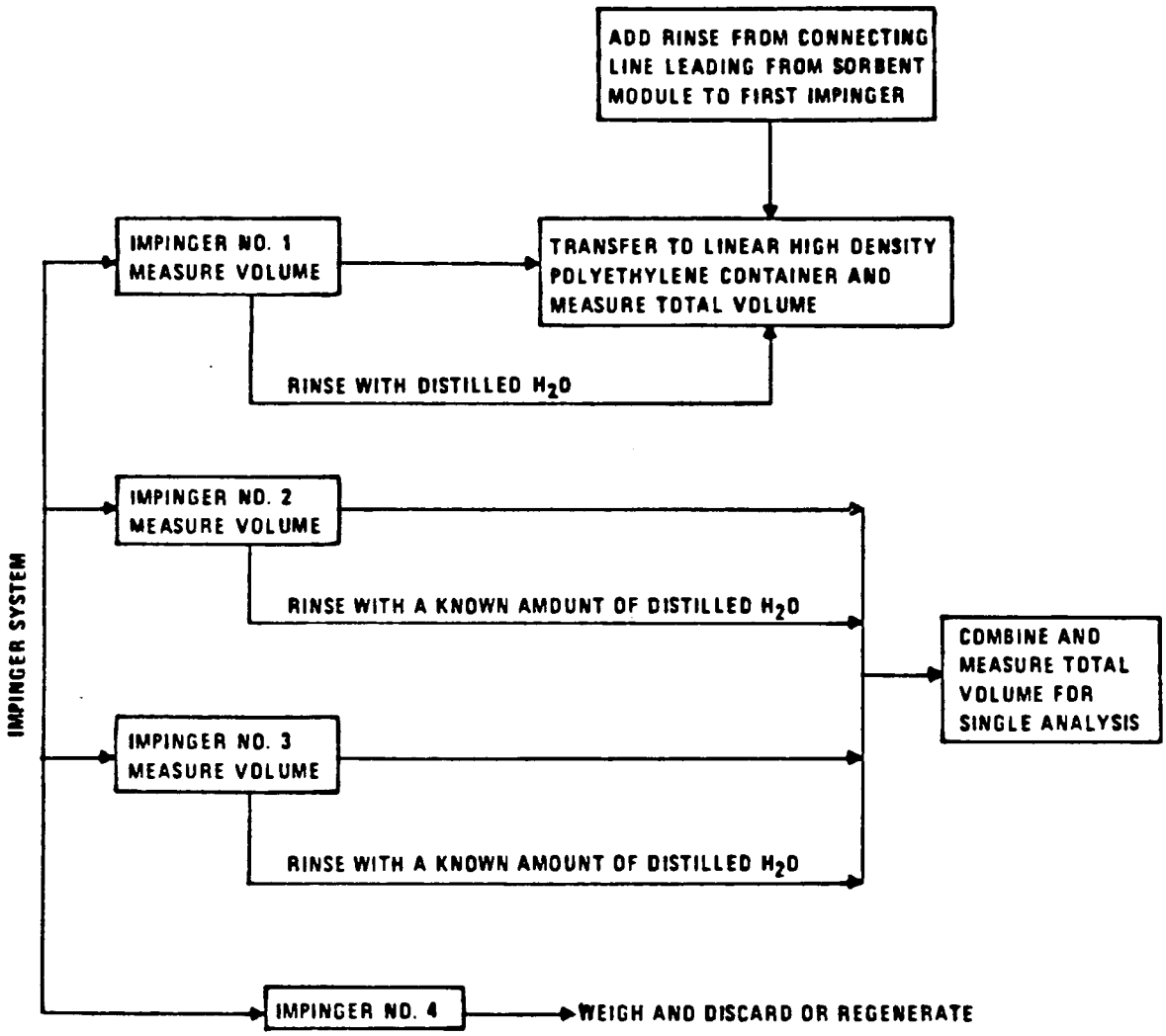


Figure 5. Sample Handling and Transfer Impingers.

5.1.1 Leaving the fan operating, open the cyclone oven door to expedite cooling. When the probe can be safety handled, disconnect from the 10-um cyclone inlet. Wipe off external particulate matter near the probe tip and place a cap over each end. The probe must remain level throughout this procedure.

NOTE: CARE MUST BE TAKEN TO AVOID TIGHTLY CAPPING TRAIN COMPONENTS AS THEY ARE COOLING FROM STACK OR OVEN TEMPERATURES. THIS WILL ELIMINATE THE POSSIBILITY OF CREATING A VACUUM INSIDE WHICH, WHEN RELEASED, MAY DISRUPT AND BACKFLUSH THE CYCLONE AND FILTER PARTICULATE CATCHES INTO ONE ANOTHER.

5.1.2 Disconnect the line joining the filter outlet to the XAD-2 module and cap off:

a. The 10-um cyclone inlet;

b. The filter holder outlet; and

c. The inlet of the line just disconnected from the filter holder outlet.

5.1.3 Disconnect the filter holder and cap the inlet. Set aside with the inlet facing upward. Cap the outlet of the 1-um cyclone. The cyclones must remain upright throughout this procedure. The cyclones can now be disconnected from one another or moved to the recovery area as a single unit.

5.1.4 Disconnect the line joining the XAD-2 module to the impinger system at the organic module outlet. Cap the organic module outlet.

5.1.5 Disconnect the silica gel impinger outlet from the vacuum line to the pumps; cap off the first impinger inlet and the fourth impinger outlet.

5.2 Nozzle, Probe, Cyclones, and Filter: The step-by-step procedures for the recovery of particulate material collected in the nozzle, probe, and cyclones, and on the filter are detailed below:

5.2.1 Carefully transfer the filter from the filter housing to its original glass Petri dish; a pair of clean blunt-tipped tweezers and a flat spatula should be used for handling the filter. Using a clean nylon-bristled brush, add any particulate material from the front half of the filter housing to the Petri dish; seal the Petri dish around the circumference with 1-in.-wide Teflon tape; store with the collected particulate material facing upward.

5.2.2 Tap and brush any particulate material adhering to the walls of the upper chamber of the 1-um cyclone into the lower cup; remove the cup and quantitatively transfer the bulk contents to a wide-mouth amber glass jar. Rinse the brush with methanol/methylene chloride (1:1 v/v) into the probe rinse container.

5.2.3 Recover the contents of the 3-um cyclone in the same manner, using a separate wide-mouth amber glass jar.

5.2.4 Recover the contents of the 10-um cyclone in the same manner, using a separate wide-mouth amber glass jar.

5.2.5 Reconnect the lower cups of each cyclone and rinse any particulate material adhering to the walls down into the cups with the methanol/methylene chloride mixture until the walls appear clean. Remove the lower cups and transfer the contents to the probe rinse container. Rinse the interconnecting tubing among the cyclones into the probe rinse in the same manner.

5.2.6 Carefully remove the probe nozzle and clean the inside surface by rinsing with the methanol/methylene chloride (1:1 v/v) from a wash bottle and brushing with a nylon-bristle brush. Brush until the rinse shows no visible particles; make a final rinse of the inside surface.

5.2.7 Rinse the probe liner (preferably with two people so as to minimize the possibility of accidental sample loss) with methanol/ methylene chloride (1:1 v/v) by tilting and rotating while spraying solvent into the upper end and allowing the lower end to drain into the sample container. Follow rinsing with brushing and rinsing from the upper to the lower end. Push the brush through the liner with a twisting action; ensure that the sample container is placed under the lower end. Brush until the rinse appears clean; perform a final rinse. Inspect the inner surface of the liner for cleanliness. Rinse any particulate material remaining on the brush into the sample container.

5.2.8 Clearly label all containers according to the coding scheme given in Table 1; cover each label completely with transparent tape; mark liquid levels and store all liquid samples on ice.

5.3 XAD-2, condensate, and organic module: Sample recovery of the entire organic module may be conducted independently from the previous steps. The step-by-step procedure for recovery of this stage is given below:

5.3.1 Rinse a 1-ft x 1-ft square of aluminum foil (dull side) with methylene chloride and allow to air dry.

5.3.2 Release the clamp joining the XAD-2 cartridge section to the upper gas conditioning system (second clamp); remove the XAD-2 cartridge from the holder and place upon the clean aluminum foil. GENTLY pry loose or unscrew (depending upon the design) the ring securing the fine mesh screen on the top of the cartridge. Remove the screen and quantitatively transfer the XAD-2 to a clean glass amber jar. A large, clean glass funnel should be used for the transfer. Rinse the inner surfaces of the cartridge and the funnel with methylene chloride as necessary to remove adhering XAD-2. Any XAD-2 that escapes onto the aluminum foil should be retrieved and added to the sample.

TABLE 1. SUGGESTED FORMAT FOR SAMPLE CODING AND IDENTIFICATION

Sample Code	Container	Size	Sample description
1C	Amber glass	100 mL, wide-mouth	1-m cyclone catch
3C	Amber glass	100 mL, wide-mouth	3-m cyclone catch
10C	Amber glass	100 mL, wide-mouth	10-m cyclone catch
PF-a,b,c,...	Glass Petri dish	>6-in. diam.	Particulate filter(s)
PR	Amber glass	1 liter	Methylene chloride/ methanol front-half rinse
PRB	Amber glass	500 mL	Methylene chloride/ methanol blank
MRX	Amber glass	1 liter	Methylene chloride back half rinse
MRXB	Amber glass	500 mL	XAD-2 resin blank
CD-LE	Amber glass	1 liter	Methylene chloride condensate extract
CD-LEB	Amber glass	500 mL	Methylene chloride blank
AR-I1	HDLP[a]	1 liter	Aqueous residue of condensate combined with first impinger catch
I1B	HDLP	500 mL	First impinger blank (distilled H_2O or other appropriate solution)
I23	HDLP	1 liter	Second and third impinger catches
I23B	HDLP	500 mL	Second and third impinger blank (distilled H_2O or other appropriate solution)

[a]HDLP = High Density Linear Polyethylene.

5.3.3 Replace the screen on the cartridge, reinsert the cartridge into the module, and reassemble the module. One person can accomplish this task by butting the lower section in its proper sealing position up against the upper section while securing the ring clamp. One or more wooden spacers approximately 1/2 in. thick are suggested for this purpose.

5.3.4 Open the condensate reservoir valve and drain the remaining condensate into the condensate storage container. Measure and record the volume and pH (using narrow-range pH paper) of the entire condensate.

5.3.5 Transfer the entire condensate to an appropriately-sized separatory funnel. Adjust the pH of the condensate (as indicated by the narrow-range pH paper) to 1-2 using ultrapure or reagent grade nitric acid. Extract the condensate three times with methylene chloride, each time with fresh portions measuring 8-10% of the total condensate volume. If the volume of the condensate is extremely large (>1800 mL), the condensate may be extracted in portions, but fresh volumes of methylene chloride must be used for each and every extraction. After each addition of methylene chloride to the separatory funnel, the funnel must be shaken with periodic venting through the stopcock to relieve any vapor pressure. For safety, the tip of the separatory funnel should <u>always</u> be directed away from the face and eyes while venting. When no further vapor pressure can be vented after shaking, the funnel should be mounted upright on a ring stand, the cap removed, the layers allowed to separate, and the methylene chloride (bottom) layer removed. If an emulsion forms equal to more than one-third the size of the solvent layer, reagent-grade sodium chloride should be added until the emulsion is broken or reduced to meet the above criterion. The emulsion interface should <u>not</u> be included as part of the methylene chloride extract.

5.3.6 Following the third extraction of the acidified condensate, adjust the pH of the aqueous residue to 11-12 with a 50% w/w solution of sodium hydroxide (as indicated by narrow-range pH paper), extract with methylene chloride in the same manner, and combine the methylene chloride extracts of the condensate at the high and low pH readings.

5.3.7 Transfer the aqueous residue from this extraction to a clean Nalgene container; retain for later addition of the first impinger solution.

5.3.8 Ensure that the condensate reservoir valve is closed, release the upper clamp, and lift the inner well halfway out of the module. Rinse the inner well into the XAD-2 module using a Teflon wash bottle containing methylene chloride, so that the rinse travels down the module and into the condensate collector. Then remove the well entirely and place to one side on a clean surface (aluminum foil prerinsed with methylene chloride). Rinse the entrance tube into the module interior; rinse the condenser wall allowing solvent to flow down through the system and collect in the condensate cup.

5.3.9 Release the central clamp again and separate the lower section (XAD-2 cartridge holder and condensate cup) from the upper.

5.3.10 Lift the empty XAD-2 cartridge halfway out of the mid-section and rinse the outer surface down into the condensate cup. Remove the cartridge completely to a clean surface (aluminum foil rinsed with methylene chloride).

5.3.11 Rinse the empty XAD-2 section into the condensate cup. Open the condensate reservoir valve and drain into the XAD-2 sample storage container (wide-mouth amber glass jar).

5.3.12 Rinse the condensate reservoir and combine the rinse with the XAD-2 resin as above.

5.3.13 Clearly label all containers according to the coding scheme presented in Table 1; cover each label completely with transparent tape; mark liquid levels and store all liquid samples on ice.

5.4 Impingers: Sample recovery from the impingers may also be accomplished independently of the other two sections of the SASS train. The procedures are described below.

5.4.1 **First impinger:**

5.4.1.1 Measure the volume of liquid in the impinger with a graduated cylinder; combine with the aqueous residue from the condensate.

5.4.1.2 Rinse the line connecting the XAD-2 module to the first impinger with Type II water; transfer the rinse to the same graduated cylinder. Rinse the impinger twice more with Type II water, combining all rinses in the graduated cylinder. Measure the total rinse volume and add to the sample. Rinse the graduated cylinder with a known amount of Type II water and add to the sample. Record all volumes on the sample recovery sheet.

5.4.2 **Second and third impingers:**

5.4.2.1 Measure and record the combined volume of liquid in the impingers in a large (1,000-mL) graduated cylinder; transfer to a clean sample storage container.

5.4.2.2 Rinse the line connecting the first and second impinger into the second impinger and the line connecting the second and third impinger into the third impinger. Transfer the rinses to the same graduated cylinder. Rinse each impinger twice again with Type II water, combining all rinses in the graduated cylinder. Measure and record the combined rinse volume and add to the sample. Rinse the graduated cylinder with a known amount of Type II water and add to the sample. Record this additional rinse volume and add to the impinger rinse volume above.

5.4.2.3 Clearly label all sample containers according to the coding scheme presented in Table 1; cover each label completely with transparent tape; mark fluid levels and store all liquid samples on ice.

5.4.3 **Fourth impinger:**

5.4.3.1 Transfer the silica gel to its original container. Weigh to the nearest 0.1 g on a triple-beam balance, and record the weight.

5.4.3.2 Discard or regenerate.

6.0 SAMPLE PREPARATION FOR SHIPMENT

6.1 Prior to shipment, recheck all sample containers to ensure that the caps are securely tightened. Seal the lids of all Nalgene containers around the circumference with vinyl tape and those of glass containers with Teflon tape. Ship all liquid samples on ice and all particulate filters with the particulate catch facing upward. Ship peroxide solutions (impinged) in a separate container.

7.0 CALIBRATION

7.1 All calibration results should be recorded on appropriate data sheets and fastened securely into a separate section in the field sampling notebook. Samples of blank data appear in 40 CFR 60 (1979), Appendix A.

7.2 Probe nozzles:

7.2.1 Probe nozzles must be calibrated before each initial use in the field. Using Vernier calipers or micrometers, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Perform ten separate measurements using different diameters; obtain the average of the ten measurements. The difference between the highest and lowest measurement results must not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they must be reshaped, sharpened, and recalibrated before reuse. Recalibration of the nozzle before each run in gas streams that are highly corrosive is strongly recommended, as the nozzle diameter may be changing slightly from one run to the next. Each nozzle must be permanently and uniquely engraved.

7.3 Pitot tube

7.3.1 If the Type-S pitot tube conforms to the construction specifications (the face openings are not visibly nicked, dented, or corroded) and the pitot tube/probe assembly meets the intercomponent spacings outlined in EPA Method 2 (see References), the pitot tube need not be calibrated to meet federal and many state testing requirements; a correction coefficient may be assigned in these cases. Some states, however, require that, once used, pitot tubes must be calibrated in a

wind tunnel. Specific state requirements such as this must be unequivocally stated prior to testing. In either case, pitot tube face openings should be inspected before each run to ensure that there has been no change in appearance since their construction or most recent calibration.

7.4 Metering system:

7.4.1 Before each initial use in the field, the metering system shall be calibrated using a standard bell prover of the proper size. (A standard bell prover is recommended for this procedure because the displacement volume of commercially available wet test meters is typically insufficient.) A meter stick should be used to indicate the distance travelled by the inner tank during the measurement. Figure 6 illustrates a suitable arrangement for the calibration. It is highly recommended that the dry gas meter be adjusted until the ratio of the dry gas meter volume to the standard bell prover volume equals 1.00 $\pm$ 0.01, to ensure that the calculated ΔH_i will result in near-isokinetic sampling rates. The calibration procedure follows:

7.4.1.1 Perform both a positive (pressure) and a negative (vacuum) leak-check of the metering system. For the negative leak-check, include only the orifice Magnehelics (reg. trademark), dry gas meter, and two vacuum pumps by removing the vacuum line connecting the fourth impinger to the vacuum pumps at the common side of the pump inlet tee, and replacing the line with a plain-end male quick connect. Tightly cap this end and leak-check in the manner outlined above under 4.4.3.11. For the positive leak-check, connect a short length of rubber tubing to the "gas exhaust" port on the SASS control module. Disconnect and vent the low side of the orifice magnehelic; close off the low-side orifice tap. Pressurize the system to 13-18 cm H_2O (5-7 in. H_2O) by blowing into the rubber tubing; pinch off the tubing and observe the magnehelic for one minute. The magnehelic reading must remain unchanged during that time period. Any loss of magnehelic pressure indicates a leak that must be corrected.

7.4.1.2 Upon obtaining satisfactory leak-checks, connect the metering system to the standard bell prover.

7.4.1.3 Using the control box Magnehelic (reg. trademark) indicator, set the pumping rate corresponding to a ΔH of 1 in. Hg. Turn the pumps off using the switches.

7.4.1.4 Record the initial temperature and pressure of the bell prover and the initial temperature and reading of the dry gas meter. Record the barometric pressure every hour.

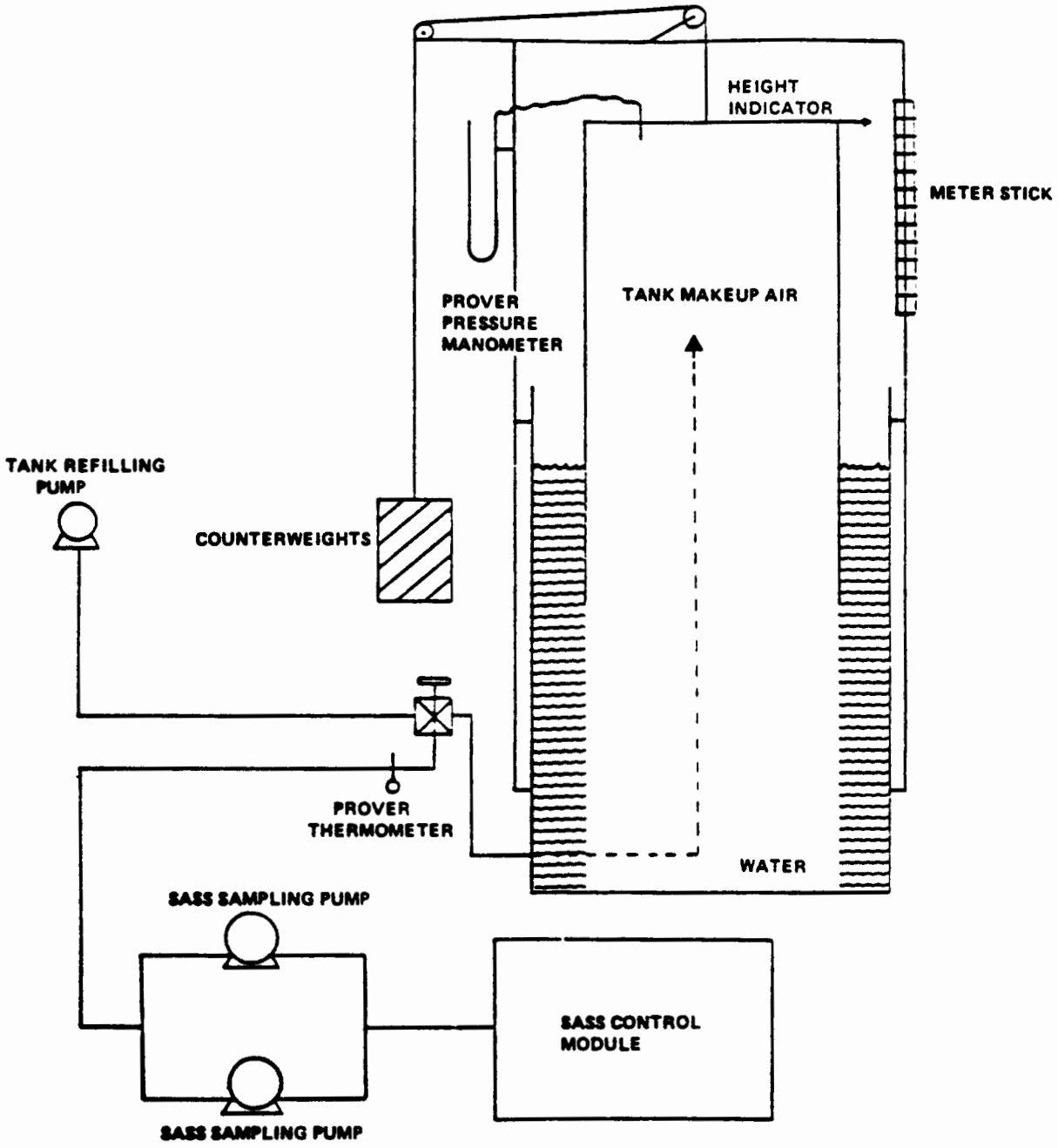


Figure 6. Schematic Diagram of Standard Bell Prover Arrangement for SASS Dry-Gas-Meter Calibration.

7.4.1.5 Disconnect the metering system and pump the inner tank of the bell prover to a convenient height. Reconnect the metering system and record the height.

7.4.1.6 Start the pumps and a stopwatch simultaneously; evacuate the tank for 3 min.

7.4.1.7 After 3 min, turn off the pumps using the switches. Record the final inner tank height, the final dry gas meter reading and temperature, and the bell prover final temperature and pressure.

7.4.1.8 Repeat steps 3-7 using ΔH settings of 2, 4, and 6 in. H_2O.

7.4.1.9 Duplicate the entire procedure as a check; repeat the entire procedure after each adjustment of the dry gas meter.

7.4.1.10 Calculate the Dry-Gas-Meter Correction Coefficient, the ratio of the volume of gas measured by the dry gas meter to the standard bell prover, both corrected to standard conditions and on a dry basis. The ratio reduces to:

$$\gamma = \frac{V_{pvr(std)}}{V_{dgm(std)}} = \frac{V_{pvr} P_{pvr} T_{dgm}}{V_{dgm} P_{dgm} T_{pvr}}$$

where:

γ = Dry gas meter correction coefficient, dimensionless;

$V_{dgm(std)}$ = Volume of gas measured by the dry gas meter on a dry basis, corrected to standard conditions, dscm (dscf);

$V_{pvr(std)}$ = Volume of gas measured by the standard bell prover on a dry basis, corrected to standard conditions, dscm (dscf);

V_{dgm} = Volume of gas measured at dry-gas-meter conditions, $m^3(ft^3)$;

= Final volume reading - initial volume reading;

V_{prv} = Volume of gas measured at standard bell prover conditions, $m^3(ft^3)$

= K_{pvr} x (difference in meter stick height readings),

where:

K_{pvr} = number of ft^3 of air displaced represented by each cm of movement along the meter stick, $m^3/cm(ft^3/cm)$;

P_{dgm} = Absolute meter pressure, mm Hg (in. Hg)

= Barometric pressure + $\Delta H/13.6$;

P_{pvr} = Absolute prover pressure, mm Hg (in. Hg)

= Barometric pressure - [(ΔP) prover manometer]/13.6;

T_{pvr} = Absolute bell prover temperature, °K (°R); and

T_{dgm} = Absolute dry-gas-meter temperature, °K (°R).

7.4.1.11 Calculate the Orifice Constants using the following equations:

a. $$Q_{mo} = (1-B_{ws})\, Q_{std}\, \frac{P_{std} T_{m(avg)}}{P_m T_{std}}$$

where:

Q_{mo} = Sampling flowrate at orifice, ft^3/min (dry);

B_{ws} = Proportion by volume of water in ambient air, dimensionless;

Q_{std} = Standard sampling flowrate for SASS, 4.0 scfm (wet);

P_{std} = Standard absolute pressure, 29.92 in. Hg;

$T_{m(avg)}$ = Average meter temperature, °R;

P_m = Absolute meter pressure (barometric pressure + $\Delta H/13.6$), in. Hg; and

T_{std} = Standard temperature, 528°R.

b. $$J_i = \frac{Q_{mo}}{A_{oi}} \left[\frac{T_{m(avg)}}{P_m M_m} R \Delta H_i 2 g_c \right]^{-1/2}$$

where:

J_i = Orifice coefficient for orifice "i";

Q_{mo} = Sampling flowrate at orifice, ft^3/min (dry);

A_{oi} = Orifice area [π(diameter)^2]/4, in.^{2};

$T_{m(avg)}$ = Average meter temperature, °R;

P_m = Absolute meter pressure (see equation above), in. Hg;

M_m = Molecular weight of air, 29.0 lb_m/lb-mole;

R = Gas law constant, 1545 ft-lb_f/°R lb-mole;

ΔH_i = Orifice "i" pressure drop, in. H_2O; and

g_c = Gravitational constant, 32.17 lb_m-ft/lb_f sec^2.

7.4.1.12 The orifice constants may be determined without the bell prover by noting the dry-gas-meter volumes obtained by pumping at 1, 2, 3, and 6 in. H_2O for 3-min periods. The obtaining of consistent values when checking orifice constants in the field may be used as a rough indication of a valid calibration during extended field use.

7.4.2 After each series of field tests, the calibration of the metering system must be checked by performing three calibration measurements at a single intermediate orifice setting at or near the average used during the field testing. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings. Calculations for the test series should then be performed using whichever calibration results in the lower value for total sample volume.

7.5 Probe heater: The probe heating system shall be calibrated before each initial use in the field and checked after each series of field tests according to the procedure outlined in APTD-0576.

7.6 Thermocouples: Each thermocouple must be permanently and uniquely marked on the casing; all mercury-in-glass reference thermometers must conform to ASTM-E-1 #63C or 63F specifications. Thermocouples should be calibrated in the laboratory without the use of extension leads. If extension leads are used in the field, the thermocouple reading at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change greater than 1.5%. Calibration for the various kinds of thermocouples proceeds as follows:

7.6.1 **Impinger and organic module thermocouples:** For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2 resin bed, a three-point calibration at ice water, room-air, and boiling-water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree within 2°C (3.6°F) of the absolute value of the reference thermometer.

7.6.2 **Dry-gas-meter thermocouples:** For the thermocouples used to indicate the dry-gas-meter inlet and outlet temperatures, a three-point calibration at ice-water, room-air, and boiling-water temperatures must be performed. The values must be within 2°C (3.6°F) of the absolute reference thermometer value at all three calibration points.

7.6.3 **Probe and stack thermocouple:** For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and boiling cooking-oil temperatures must be performed; it is highly recommended that room-air temperature be added as a fourth calibration point. If the absolute values of the reference thermometer and the thermocouple agree within 1.5% at each of the calibration points, a calibration curve (equation) may be constructed (calculated), and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

7.7 Barometer: Adjust the field barometer initially and before each test series to agree within 2.5 mm Hg (0.1 in. Hg) of the mercury barometer, or within the station barometric pressure value reported by a nearby National Weather Service station and corrected for elevation.

7.8 Triple-Beam Balance: Calibrate the triple beam balance before each test series using Class-S standard weights; the weights must be within 0.5 g of the standards, or the balance adjusted to meet these limits.

7.9 Analytical Balance: Calibrate the analytical balance with Class-S weights before initially tare-weighing each set of filters. The balance must agree or be adjusted to within 2 mg of the standards. Run at least one standard each time one or more of the filters is reweighed.

8.0 CALCULATIONS

8.1 Dry gas volume:

8.1.1 From the SASS run sheet, average the dry-gas-meter temperatures and orifice pressure drops readings throughout the run. Calculate the Volume of Dry Gas Sampled at standard conditions (20°C, 760 mm Hg [528°R, 29.92 in. Hg]) using the equation:

$$V_{m(std)} = V_m Y \frac{(T_{std})}{T_m} \frac{(P_{bar} + (\Delta H/13.6))}{P_{std}}$$

$$= K_1 V_m Y \frac{(P_{bar} + (\Delta H/13.6))}{T_m}$$

where:

$V_{m(std)}$ = Volume of dry gas sampled at standard conditions, dscm (dscf);

V_m = Volume of dry gas sampled at dry-gas-meter conditions, dcm (dcf);

γ = Dry-gas-meter calibration factor, dimensionless;

T_m = Average dry-gas-meter temperature, °K (°R);

T_{std} = Standard absolute temperature, °K (°R);

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg);

P_{std} = Standard absolute pressure, mm Hg (in. Hg);

ΔH = Average orifice pressure drop during the sampling run, mm H_2O (in. H_2O); and

K_1 = 0.358°K/mm for metric units
= 17.64°R/in. Hg for English units.

8.1.2 The above equation must be modified whenever the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-checks or leak-checks made prior to component changes) exceeds the maximum allowed. The modification follows:

8.1.2.1 Case I (No component changes have been made during the sampling run, and the allowable leakage rate has been exceeded during the post-test leak-check): Replace V_m with the expression:

$$V_m - [(L_p - L_a)\theta]$$

where:

L_p = Leakage rate observed during post-test leak-check, m^3/min (cfm);

L_a = Maximum allowed leakage rate, 0.0014 m^3/min (0.05 ft^3/min); and

θ = Total sampling time, min.

8.1.2.2 Case II (One or more component changes made during the sampling run, and the allowable leakage rate has been exceeded

during one or more of the leak-checks prior to component changes or during the post-test leak-check): Replace V_m with the expression:

$$V_m - \sum_{i=1}^{n} \left[\theta_{i-1}(L_i - L_a) - \theta_p(L_p - L_a) \right]$$

where:

L_i = Leakage rate observed prior to "i^{th}" component change if the allowable leakage rate has been exceeded while sampling with the "i^{th}" component, m^3/min (cfm);

L_a = Maximum allowed leakage rate, 0.0014 m^3/min (0.05 ft^3/min);

θ_{i-1} = Sampling time interval between the successive component changes in which the allowable leakage rate has been exceeded, min;

L_p = Leakage rate observed during post-test leak-check, if the allowable leakage rate has been exceeded, m^3/min (cfm); and

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, if the allowable leakage rate has been exceeded during the post-test leak-check, min.

8.2 Moisture content:

8.2.1 Calculate the Volume of Water Vapor at standard conditions:

$$V_{w(std)} = \left[\frac{\rho_w}{M_w} \right] \left[\frac{RT_{std}}{P_{std}} \right] = K_2 V_{lc}$$

where:

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, dscm (dscf);

V_{lc} = Volume of liquid collected in the condensate reservoir added to the net increase in impinger solution volumes and silica gel weight gain during the run, mL;

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL);

M_w = Molecular weight of water, 18.0 g/g-mole (lb/lb-mole);

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole);

T_{std} = Standard absolute temperature, °K (°R);

P_{std} = Standard absolute pressure, mm Hg (in. Hg); and

K_2 = 0.001333 m^3/mL for metric units
= 0.04707 ft^3/mL for English units.

8.2.2 Calculate the Stack Gas Moisture Content (equal to B_{ws} x 100 for conversion to percent):

$$\%M = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} = B_{ws} \times 100$$

where:

B_{ws} = Proportion of water vapor in the gas stream by volume, dimensionless;

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, dscm (dscf); and

$V_{m(std)}$ = Volume of gas measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

8.2.3 In saturated or water-droplet-laden gas streams, make two calculations of the moisture content, one from the total volume of liquid collected in the train and one from the assumption of saturated gas-stream conditions. Use whichever method results in the lower value. To determine the moisture content based upon saturated conditions, use the average stack gas temperature in conjunction with: (1) a psychrometric chart, correcting for difference between the chart and the absolute stack pressure; or (2) saturation vapor pressure tables.

8.3 Particulate concentration:

8.3.1 Calculate the Unit Methanol/Methylene Chloride Blank Correction for all front-half samples:

$$C_{mm} = \frac{M_{mm}}{V_{mm}\rho_{mm}}$$

where:

C_{mm} = Methanol/methylene chloride blank correction, mg/g;

M_{mm} = Mass of methanol/methylene chloride after evaporation, mg;

V_{mm} = Volume of methanol/methylene chloride used in wash, mL; and

p_{mm} = Density of 50:50 mix of methanol/methylene chloride, mg/mL (see labels on bottles).

8.3.2 Calculate the Total Methanol/Methylene Chloride Blank Weight Correction for each individual front-half sample:

$$W_{mm} = C_{mm} V_{mm} \rho_{mm}$$

where:

W_{mm} = Weight of residue in methanol/methylene chloride front-half wash, mg;

C_{mm} = Methanol/methylene chloride unit blank correction, mg/g;

V_{mm} = Volume of methanol/methylene chloride used for front-half wash, mL; and

ρ_{mm} = Density of 50:50 mixture of methanol and methylene chloride, mg/mL.

8.3.3 Calculate Total Particulate Weight:

$$W_p = (W_{pf\text{-}a} + W_{pf\text{-}b} + \ldots\ldots) + (W_{10c} + W_{3c} + W_{1c}) + (W_{pr} - W_{mm})$$

where:

W_p = Total particulate weight, mg;

$W_{pf\text{-}a+\ldots}$ = Particulate weight from filter Pf-a + Pf-b + ... ;

W_{10c}, W_{3c}, W_{1c} = Particulate weight catch from the 10-, 3-, and 1-um cyclones, respectively, mg;

W_{pr} = Weight of front-half rinse residue before blank correction, mg; and

W_{mm} = Methanol/methylene chloride blank weight correction, mg.

8.3.4 Calculate the Total Particulate Concentration:

$$C_p = (0.001\ g/mg)\ (W_p/V_{m(std)})$$

where:

C_p = Concentration of particulate material in the stack gas, g/dscm (gr/dscf);

W_p = Weight of particulate material collected during run, mg; and

$V_{m(std)}$ = Volume of gas sampled, dscm (dscf).

8.3.5 To convert the above concentration to units of gr/ft^3 or lb/ft^3 for comparison with established or projected values, the following conversion factors are useful:

From:	To:	Multiply By:
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft	2.205×10^{-3}
g/ft^3	g/m^3	35.315

8.4 Concentration of organic material:

8.4.1 Calculate the Volumetric Flow Rate (Q_{sd}) during the run. Determine the average stack gas velocity and volumetric flow rate from actual run data in the same manner that these were calculated during preliminary determinations (see Paragraph 4.3).

8.4.2 Calculate the POHC Concentration:

$$C_{pohc} = \frac{M_{pohc}}{Q_{sd}} = \frac{M_{cd\text{-}le} + M_{mrx}}{Q_{sd}}$$

where:

C_{pohc} = Concentration of POHCs in stack gas, ug/dscm;

M_{pohc} = Total mass of POHCs collected in XAD-2 and organic module rinse, and in the condensate extract, ug;

$M_{cd\text{-}le}$ = Mass of POHCs extracted from the condensate (corrected for methylene chloride blank extraction residue), ug;

M_{mrx} = Mass of POHCs extracted from the XAD-2 sorbent and organic module rinse (corrected for methylene chloride blank extraction residue), ug; and

Q_{sd} = Volumetric flow rate during the run, dscm.

8.5 Isokinetic variation:

8.5.1 Having calculated T_s, $V_{m(std)}$, V_s, A_n, P_s, and B_{ws}, determine the Isokinetic Variation using the equation:

$$I = K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta (1-B_{ws})}$$

where:

I = Isokinetic variation, %;

T_S = Absolute average stack gas temperature, °K (°R);

$V_{m(std)}$ = Volume of gas sampled, dscm (dscf);

P_S = Absolute stack gas pressure, mm Hg (in. Hg);

V_S = Stack gas velocity, m/sec (ft/sec);

A_n = Cross-sectional area of nozzle, m^3 (ft^3);

θ = Net sampling time, min;

B_{ws} = Proportion of water vapor in gas stream by volume, dimensionless; and

K_4 = 4.320 for metric units
= 0.09450 for English units.

8.5.2 For the accuracy of Level 1 requirements (factor of 3) for measured particulate emissions, the isokinetic variation must be within 70-150%.

8.6 Cyclone particle-size cutoff diameter:

8.6.1 The particle-size cutoff diameter represents that particle diameter (assuming spherical particles of unit density) at which the cyclone exhibits 50% collection efficiency; it is expressed as the "d_{50}." The range of particle size collected in each cyclone and on the filter is dependent upon the operating temperature and flow rate through each of

these components. The particle-size cutoff diameters of 10, 3, and 1 um in the cyclones are the result of calibration of these at 400°F and 4.0 scfm (6.5 acfm). When the determined isokinetic sampling rate is not 4.0 scfm, or when it is necessary to maintain a constant subisokinetic sampling rate (still within the limits of Level 1 accuracy) during the SASS run, the particle-size cutoff diameters for the cyclones must be extrapolated.

8.6.2 Existing calibration data is insufficient to determine exact mathematical relationships for variations of particle-size cutoff diameter with temperature and with volumetric flow rate. The best estimates (McCain, 1983) suggest that a square, and an inverse square root dependence, respectively, exist; the extrapolation equation is presented below.

8.6.2.1 Calculate the Gas Viscosity from the equation:

$$\mu = (1.68 \times 10^{-4}) + (2.292 \times 10^{-7})\ (T)$$

where:

μ = Gas viscosity, poise; and

T = Gas temperature, °F.

8.6.2.2 Extrapolate the Particle Size Cutoff Diameter from:

$$D_{T_a,F_a} = D_{400,4.0} \frac{\left[\frac{\mu_{400}}{\mu_{T_a}}\right]^2}{\left[\frac{V_{4.0}}{V_{F_a}}\right]^{1/2}} = D_{400,4.0} \frac{3.37\sqrt{V_{F_a}}}{\mu^2 T_a}$$

where:

D_{T_a,F_a} = Particle size cutoff diameter at cyclone operating a temperature and flow rate, um (note that the volumetric flow rate must be corrected to standard conditions);

$D_{400,4.0}$ = Particle size cutoff diameter at an operating temperature of 400°F and flow rate of 4.0 scfm, um;

μ_{400} = Gas viscosity at 400°F, poise;

μT_a = Gas viscosity at operating conditions, poise;

$V_{4.0}$ = Cyclone volumetric flow rate of 4.0 scfm; and

V_{F_a} = Cyclone volumetric flow rate at operating conditions, scfm.

This equation reduces to:

1. $$\frac{33.7\sqrt{V_{F_a}}}{\mu T_a^2}$$ **for the 10-um cyclone,**

2. $$\frac{10.1\sqrt{V_{F_a}}}{\mu T_a^2}$$ **for the 3-um cyclone,**

3. $$\frac{3.37\sqrt{V_{V_a}}}{\mu T_a^2}$$ **for the 1-um cyclone,**

8.7 Cumulative particulate weight percent less than calculated size:

8.7.1 Divide the weight collected in the individual cyclones and on the filter by the total weight of particulate collected; express these as a percentage, using the following equations:

$$\% W_{pf} = \frac{W_{pf\text{-}a} + W_{pf\text{-}b} + \ldots}{W_p} \times 100$$

$$\% W_{10c} = \frac{W_{10c}}{W_p} \times 100$$

$$\% W_{3c} = \frac{W_{3c}}{W_p} \times 100$$

$$\% W_{1c} = \frac{W_{1c}}{W_p} \times 100$$

where:

W_p = Total particulate weight collected, mg;

$W_{pf} = W_{pf-a} + W_{pf-b} + \ldots$

= Particulate weight collected on filters PF-a + PF-b, etc., mg;

W_{10c} = Particulate weight collected in 10-um cyclone, mg;

W_{3c} = Particulate weight collected in 3-um cyclone, mg;

W_{1c} = Particulate weight collected in 1-um cyclone, mg; and

100 = Conversion to percent.

8.7.2 Calculate the Cumulative Weight Percent Less than the Calculated Particle Size Cutoff Diameter by adding, to each weight percent, the weight percent of all fractions having a smaller particle- size cutoff diameter. Tabulate the data, using the form below as an example:

PRESENTATION OF SASS PARTICLE SIZING DATA

Stage	Weight % Collected in Stage	Cumulative Weight % Less than Calculated Particle Size Cutoff Diameter	Calculated Particle Size Cutoff Diameter
10-um cyclone			
3-um cyclone			
1-um cyclone			
Glass fiber filter			

9.0 REFERENCES

9.1 References

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METHOD 0023A

SAMPLING METHOD FOR POLYCHLORINATED DIBENZO-*p*-DIOXINS AND POLYCHLORINATED DIBENZOFURAN EMISSIONS FROM STATIONARY SOURCES

1.0 SCOPE AND APPLICATION

1.1 This method describes the sampling procedure to be used for determining stack emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from stationary sources. The air sample is collected and analyzed by the determinative portion of Methods 8280 or 8290. This method describes the procedures for sampling and calculating results. This method may be modified to allow simultaneous sampling and analysis for polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), or semivolatile organic compounds (SVOCs). However, specific approval is required for this modification, and detailed modification of the methodology is required.

1.1.1 This method is a revision of Method 23 (see Ref. 10).

1.1.2 The surrogates and recovery standards include the standards listed in Methods 8280 and 8290.

1.1.3 The method refers to specific techniques described in Methods 1, 2 and 5 (see Ref. 10). Analysts should obtain copies of those methods prior to sampling.

1.2 This method is restricted to use by or under the supervision of analysts experienced in the use of air sampling methods and the analysis of PCDDs, PCDFs, PCBs, PAHs, and SVOCs from the components of Method 0010 trains. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.3 Safety - The laboratory should develop a strict safety program for the handling of PCDDs and/or PCDFs.

1.3.1 2,3,7,8-TCDD has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The analyst must be aware of the potential for inhalation and ingestion. It is recommended that such samples be processed in a confined environment, such as a hood or a glove box. Personnel handling these types of samples should wear masks fitted with charcoal filters to prevent the inhalation of airborne particulates.

1.3.2 The toxicity or carcinogenicity of each reagent used in this method is not precisely defined. However, each chemical should be treated as a potential health hazard, and exposure to these chemicals kept to a minimum. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be made available to all personnel involved in the sampling and chemical analysis of samples suspected to contain PCDDs/PCDFs. Method 8290 and References 7, 8, and 9 give additional information on laboratory safety.

2.0 SUMMARY OF METHOD

2.1 Gaseous and particulate PCDDs/PCDFs are isokinetically withdrawn from an emission source and collected in a multicomponent sampling train. The collection components consist of the front half glassware surfaces (nozzle, probe, and front half filter holder), the glass fiber filter, the back half glassware surfaces (back half filter holder and condenser coil) and the solid sorbent (XAD-2®) module.

2.2 Following sampling the glass collection components are rinsed. The PCDD/PCDF are then extracted from the front half rinses and filter and another separate extraction is performed on the XAD-2® and back half rinses.

2.3 The filter and XAD-2® extracts are then analyzed separately. Surrogate recoveries are determined for both fractions. The analysis is performed using high resolution gas chromatography (HRGC) and high resolution mass spectrometry (HRMS), using the procedures of Method 8290.

3.0 INTERFERENCES

3.1 The use, in this method, of high resolution mass spectrometry with high resolution capillary gas chromatography avoids the interference from polychlorinated biphenlys and polychlorinated diphenyl ethers which could be serious with lower resolution techniques.

3.2 Very high amounts of other organic compounds in the matrix will interfere with the analysis. Extensive column-chromatographic cleanup has been introduced into typical HRGC/HRMS analytical methodology to minimize matrix effects due to high concentrations of organic compounds.

3.3 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by preparing and analyzing laboratory method blanks.

Glassware must be cleaned thoroughly before using. A procedure which has been found to be effective is given in Sec. 6.1.4, but any protocol which consistently results in contamination-free glassware is acceptable.

3.3.1 The use of high purity reagents and solvents helps to minimize interference problems in sample analysis.

4.0 APPARATUS AND MATERIALS

The following section describes all the sampling equipment and the associated performance specifications necessary to collect a gas sample from a stationary source according to Method 0023.

4.1 Sampling train - A schematic diagram of the sampling train is shown in Figure 1. This train configuration has been adapted from Method 5 (Reference 10) with the addition of condenser, XAD-2® trap and filtration-coil connecting glassware. Sealing greases must not be used in assembling the train. Complete sampling systems are commercially available that have been developed to meet all the EPA equipment design specifications. The following equipment is required.

4.1.1 Nozzle - The nozzle should be made of quartz or borosilicate glass. Stainless steel nozzles should not be used. The taper angle should be ≤ 30°, with taper on the outside to preserve a constant inside diameter (ID). The nozzle ID should be determined in order to sample isokinetically at a rate that allows collection of an adequate sample volume. The minimum sample volume should be determined to allow appropriate detection limits to be achieved (see Sec. 6.2.3).

4.1.2 Probe liner - The sampling probe liner should be constructed of borosilicate or quartz glass tubing. The typical outside diameter (OD) used by sampling equipment manufacturers is about 16 mm, encased in a stainless steel sheath with an OD of 25.4 mm. Either borosilicate or quartz glass liners may be used for stack temperatures up to about 480°C, but quartz glass liners should be used at higher stack temperature [480 to 900°C].

4.1.3 Probe sheath and heating system - A stainless steel or equivalent probe sheath should be used to house the probe liner and heating system. The probe heating system should be capable of maintaining probe gas temperatures at the probe exit of 120°C ± 14°C during sampling. This temperature should be verified by placing a thermocouple temperature sensor against the outer surface of the probe liner at least 2 feet upstream of the filter oven. Temperature readings should be recorded during sampling.

4.1.4 Glass cyclone - A glass cyclone may be used between the probe and filter holder for high particulate concentrations. A cyclone, if used, should be rinsed and recovered with the front half of the train.

4.1.5 Filter holder - A filter holder of borosilicate glass with a Teflon® frit filter support should be used. The holder design should provide a positive seal against leakage from the outside or around the filter. The holder should be durable, easy to load, leak-free in normal applications, and is positioned immediately following the probe (or cyclone, if used) with the filter placed toward the flow.

4.1.6 Filter heating system - Any heating system may be used which is capable of maintaining the filter holder at 120°C ± 14°C during sampling. Other temperatures may be specified by a subpart of the regulations or approved for a particular application. A gauge capable of measuring temperatures to within 3°C should be provided to monitor the temperature around the filter during sampling.

4.1.7 Sample transfer lines - A sample transfer line may be used if needed to direct sample flow from the probe to the filter or from the filter to the condenser. The probe-to-filter line should be insulated and heated so that gas exit temperatures are 120°C ± 14°C. The filter-to-condenser line should be insulated and oriented with the downstream end lower than the upstream end so that any condensate will flow away from the filter and into the condenser. These lines should be constructed of Teflon® or glass and should be recovered with their respective rinse fractions (front half or back half).

4.1.8 Condenser - A multi-coil water-cooled glass condenser should be used to cool the sample gas prior to entry into the sorbent module. The orientation of the condenser should be vertical.

4.1.9 Sorbent module - The glass water-cooled container configured to hold the solid sorbent (XAD-2®) should contain a minimum of 20 g of XAD-2® and may contain as much as 40 g. A schematic diagram is shown in Figure 2. A single piece condenser-trap can be used if desired. The sorbent trap configuration should be vertical so that condensate drains from

the condenser through the sorbent and so that channeling of the gas flow does not occur. The connecting fittings should form leak-free, vacuum tight seals. Sealant greases should not be used in the sampling train. A coarse glass or Teflon® frit along with glass wool plugs is included to retain the sorbent. The tester may engrave a unique identification number for inventory and sample tracking.

4.1.10 Impinger trains - Four impingers should be connected in series with leak-free ground-glass fittings or any similar noncontaminating fittings. The first impinger should be a short stem (knock out) version. The second impinger should be a Greenburg-Smith impinger with the standard tip and plate. The third and fourth impingers should be the Greenburg-Smith design modified so that the glass tube has an unconstricted 13 mm ID and extends to within 13 mm of the flask bottom. The fourth impinger outlet connection should allow insertion of a thermometer capable of measuring ± 1°C of true value in the range of 0 to 25°C.

4.1.11 Water circulating bath - A bath and pump circulating system which is capable of providing chilled water flow to the condenser and sorbent trap water jackets should be used. Typically a submersible pump is placed in the impinger ice water bath so that the ice water contained there can be used. The function of this system should be verified by measuring sorbent trap gas entrance temperature $\leq$20°C.

4.1.12 Pitot tube - The pitot tube, preferably of Type S design, shall meet the requirements of Method 2. The pitot tube is attached to the probe as shown in Figure 1. The proper pitot tube-sampling nozzle configuration for prevention of aerodynamic interference is shown in Figures 2.6 and 2.7 of Method 2. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Sec. 4 of Method 2.

4.1.13 Differential pressure gauge - The differential pressure gauge should be an inclined manometer or the equivalent as described in Method 2. Two gauges are required: one gauge to monitor the stack velocity pressure (ΔP), and the other to measure the orifice pressure differential (ΔH).

4.1.14 Metering system - The metering system should consist of a dry gas meter with 2% accuracy, a vacuum pump, a vacuum gauge, orifice meter, thermometers or thermocouples capable of measuring ± 3°C of true value in the range of 0 to 90°C; and related equipment as shown in Figure 1. Thermocouples should be used to monitor the temperature at the following sampling train locations:

- stack gas
- probe liner
- filter holder
- sorbent trap entrance
- silica gel impinger exit
- dry gas meter inlet and
- dry gas meter outlet.

Other metering systems capable of maintaining isokinetic sampling rates within 10% and determining sample volumes to within 2% may be used if approved. Sampling trains with metering systems designed for sampling rates higher than those described in APTD-0581 and APTD-0576 (Air Pollution Technical Document, see references) may be used if the above specifications can be met. When the metering system is used with a pitot tube, the system should permit verification of an isokinetic sampling rate through the use of a nomograph or by calculation.

4.1.15 Barometer - A mercury (Hg), aneroid, or other barometer capable of measuring atmospheric pressure to within ± 2.5 mm Hg is needed. A preliminary check of a new barometer should be made against a mercury-in-glass barometer or the equivalent. The absolute barometric pressure may be obtained from a nearby weather service station and adjusted for elevation difference between the station and the sampling point. Either subtract 2.5 mm Hg from the station value for every 30 m elevation increase or add the same for an elevation decrease. If the barometer cannot be adjusted to agree within 0.1 in. Hg of the reference barometric pressure, it should be repaired or discarded.

4.1.16 Gas density determination equipment - The equipment necessary for conducting Methods 2 - 4 for determining stack gas flow, molecular weight and moisture content, respectively, should be used. Required measurements include stack gas velocity and static pressure; gas temperature; concentrations of O_2, CO_2, and N_2 (by difference), metered gas volumes and meter temperatures and pressure; and condensate weight gain collected by the impinger train. All equipment should meet Methods 2 through 4 requirements.

4.2 Sample recovery equipment

4.2.1 Fitting caps - Ground glass or cleaned aluminum foil to cap the exposed sections of the train.

4.2.2 Wash bottles -Teflon® .

4.2.3 Probe-liner, probe-nozzle, and filter-holder brushes - These should be constructed with nylon or Teflon® bristles with precleaned stainless steel or Teflon® handles. The probe brush should have extensions of stainless steel or Teflon® at least as long as the probe. The brushes should be properly sized and shaped to brush out the nozzle, probe liner, and front half filter holder.

4.2.4 Filter storage container - Typically a glass petri dish sealed with Teflon® tape is used. Petri dishes should be cleaned according to glassware cleaning procedures listed in this method (Sec. 6.1.4).

4.2.5 Balance - This balance is used for measuring weight gain of the impingers and sample bottle weights as well. Typically a 0 to 2000-g balance is used. The balance should be accurate to within 0.5 g, verified with ASTM Class 1 (Class S) weights.

4.2.6 Aluminum foil - Heavy duty cleaned by rinsing three times with methylene chloride and once with toluene, stored in pre-cleaned glass petri dish or glass jar.

4.2.7 Graduated cylinder - Glass, 250-mL, with ± 1 mL resolution (this cylinder can be used for impinger volume determinations in place of the balance).

4.2.8 Glass sample storage container - Amber glass bottle for sample glassware washes, 500- or 1000-mL, with leak-free Teflon® -lined caps. The bottles should be either purchased as precleaned or cleaned according to glassware cleaning procedures listed in this method (Sec. 6.1.4).

5.0 REAGENTS

5.1 Filters - Glass fiber filters, without organic binder, exhibiting at least 99.95% efficiency (< 0.05% penetration) on 0.3 µm dioctyl phthalate smoke particles. One filter from each batch is tested for contamination using the procedure in Sec. 5.1.2. If the filter fails the test, then all filters must be cleaned and retested before their initial use according to the following procedures.

5.1.1 Precleaning - Place no more than 50 filters in a Soxhlet extraction apparatus. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool. Remove the filters and dry under a clean nitrogen (N_2) stream. Store the filters in cleaned glass petri dishes or amber glass bottles sealed with Teflon® tape or Teflon® -lined caps prior to using them.

5.1.2 As a quality control check prior to the field test, take one precleaned filter and perform Soxhlet extraction with toluene for 16 hours. Remove the toluene extract and analyze according to Method 8290. No analytes may be observed above the detection limit.

5.1.3 Filter surrogate spike solution - As stated in Sec. 7.3.3, this method calls for both the filter and the XAD-2® sorbent to be spiked with the same set of isotopically labeled PCDD/PCDF standards. Surrogate spikes are added to the sorbent prior to sampling and to the filter immediately before the sample extraction. The filter and XAD-2® fractions (including the associated glassware rinses) are extracted separately and analyzed separately. The surrogate standards listed in Table 1 should be used for both the filter spike and sorbent spike.

5.1.4 To ensure proper filter spiking, the isotopically-labeled standard solution, which is normally at a concentration of 0.1 ng/µL, is diluted to 0.004 ng/µL with nonane, for a dilution factor of 25. This spiking solution will be used to spike the surface of the filter as discussed in Sec. 7.3.1.

5.2 Sorbent resin - Amberlite XAD-2® resin. XAD-2® may be purchased precleaned or cleaned by the laboratory. If the sorbent has not been precleaned, a cleaning procedure capable of producing resin meeting the quality control check in Sec. 5.2.1.8 shall be implemented. The procedure given below has been found to produce excellent results.

5.2.1 Sorbent resin cleaning procedure

5.2.1.1 Place the sorbent resin in a clean beaker and rinse with reagent water. Discard the rinse. Fill the beaker a second time with reagent water and allow the resin to stand overnight. Discard this second rinse.

5.2.1.2 Place the sorbent resin in an all-glass thimble of a large Soxhlet extractor. The sorbent resin will float when in contact with methylene chloride. Therefore, add a glass wool plug on top of the resin in the thimble, and weight the glass wool plug down with a stainless steel ring that fits inside the thimble.

5.2.1.3 Place the thimble filled with resin into the Soxhlet extractor, add organic-free reagent water to the distilling flask, apply heat, and extract the resin for 8 hours.

5.2.1.4 Allow the Soxhlet extractor to cool, discard the water, and add methanol to the extractor. Apply heat and extract for 22 hours.

5.2.1.5 Again allowing the extractor to cool, drain off the methanol, replace it with methylene chloride. Make sure that the stainless steel ring and glass wool plug are still in place and extract for 22 hours.

5.2.1.6 Extract the resin a fourth time, using toluene as the extraction solvent, for 22 hours.

5.2.1.7 Following the toluene extraction, the sorbent resin must be dried under a stream of clean dry nitrogen or other inert gas. This may be accomplished by transferring the resin to a large diameter glass column and flowing the gas through the column. The gas may be heated to less than 40°C, using a steam bath or other appropriate heat source. Continue the inert gas flow through the resin until all the residual solvent is removed. The flow rate should be sufficient to agitate the resin particles, but not so excessive as to cause the particles to fracture.

5.2.1.8 A quality control check should be conducted on the cleaned sorbent using HRGC/HRMS techniques (Method 8290). Typically, a method blank conducted previously on the same lot of sorbent can serve this purpose.

5.2.2 Sorbent resin surrogate spike solution - The-XAD-2® sorbent is spiked with isotopically labeled PCDD/PCDF standards prior to sampling (surrogate spikes).

5.3 Glass wool - Cleaned by sequential immersion in three aliquots of methylene chloride and one aliquot of toluene, dried in a 110°C oven, and stored in a toluene-washed glass jar with a Teflon® -lined screw cap.

5.4 Organic-free reagent water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.5 Silica gel - Indicating type, 6 to 16 mesh. If previously used, dry at 175°C for two hours. New silica gel may be used as received. Alternatively, other types of desiccants may be used, provided that appropriate performance has been demonstrated.

5.6 Recovery solvents - Solvents must be pesticide quality or equivalent.

5.6.1 Acetone, CH_3COCH_3

5.6.2 Methylene chloride, CH_2Cl_2

5.6.3 Toluene, $C_6H_5CH_3$

6.0 SAMPLING COLLECTION, PRESERVATION, AND PREPARATION

This section addresses preparation and collection procedures for sampling.

6.1 Laboratory preparation

6.1.1 Filters. (See Sec. 5.1.)

6.1.2 Sorbent trap. (See Sec. 5.2.)

6.1.3 Glass wool - Precleaning and storage. (See Sec. 5.3.)

6.1.4 Glassware - All glass components of the train should be cleaned thoroughly. The following procedure has been found to be effective, but any protocol which consistently results in contamination-free glassware is acceptable.

Soak all glassware in hot soapy water (Alconox® or equivalent).
Rinse with tap water to remove soap.
Rinse with distilled/deionized H_2O (three times).
Bake at 400°C for 2 hours.
Rinse with methylene chloride (pesticide grade) (three times).
Rinse with toluene (pesticide grade) (three times).
Cap glassware with clean glass caps or cleaned aluminum foil.
Mark cleaned glassware with color-coded identification stickers.
Rinse glassware immediately before using with acetone and methylene chloride.

6.1.5 Because probe liners do not usually fit in glassware baths or ovens, they may be rinsed three times with methylene chloride followed by three rinses with toluene, and sealed during transport.

6.2 Preliminary field determinations

6.2.1 Sample site - The sampling site and the minimum number of sampling points should be selected according to Method 1 or as specified by the Agency. The stack static pressure, temperature, and range of velocity pressures (ΔPs) should be determined using Method 2. The stack gas moisture content should be determined using Method 4, its alternatives, previous data, or an engineering estimate. Stack gas O_2 and CO_2 concentrations should be estimated and dry molecular weight should be calculated. These parameters are used to estimate the isokinetic sampling rate settings.

6.2.2 Nozzle size - The nozzle size should be based on the range of velocity pressures so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates.

6.2.3 Sampling duration - The total length of sampling time needed to obtain the identified minimum sample gas volume is determined by comparing the anticipated average sampling rate with the volume requirement. (Average sampling rate should be within 0.5 to 0.75 cfm.) The same time should be allocated to all traverse points defined by Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half minute.

6.2.3.1 Calculation of length of the sampling duration - The minimum sampling time required to achieve a minimum sample volume and the corresponding detection limit (DL) are given below.

$$\text{Minimum sample time} = \frac{\text{analytical DL}}{\text{(Sample Rate) x (desired gas conc. DL)}}$$

6.2.3.2 The following calculation is for a single isomer (i.e., 2,3,7,8-TCDF). Detection limits for other isomers may need to be calculated as well. For this example, it will be assumed that the analytical detection limit is 0.5 ng (actual analytical detection limit will need to be specified for each test program).

6.2.3.3 At a sampling rate of 0.014 m^3/min (0.5 cfm), the sample volume per hour will be 0.85 m^3/h. Assuming a desired stack gas concentration detection limit to be 0.1 ng/m^3, the minimum sample time required to collect 0.5 ng at concentration in the stack of 0.1 ng/m^3 would be:

$$\text{Minimum sample time} = \frac{0.5 \text{ ng}}{0.85 \text{ m}^3\text{/h} \times 0.1 \text{ ng/m}^3} = 6.25 \text{ h}$$

6.2.3.4 The total sampling time should be greater than or equal to the minimum total sampling time required to achieve the necessary detection limit. In addition, the sampling time per point should be greater than 2 min (greater minimum time interval may be specified by the Agency), and the sample volume corrected to standard conditions shall exceed the required minimum total gas sample volume.

6.3 Calibration

Calibration of the apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures for the sampling apparatus listed in this section can be found in Method 5 and Method 0010. Table 4 summarizes the quality assurance functions for the calibrations.

6.3.1 Metering system

6.3.1.1 Full dry gas meter calibration - The dry gas meter (DGM) in the meter console of the sampling system should be fully calibrated against a primary standard meter (wet test meter or spirometer) or alternatively against a second reference meter (dry gas meter or critical orifice) that has been calibrated against a primary standard meter. The procedure can be found in Method 5.

6.3.1.2 Post-test DGM calibration check - Following the test program, the full calibration factor or meter Y should be checked by performing a post-test DGM calibration check. Any secondary reference meters can be used. Three calibration runs are conducted at the maximum vacuum reached during the testing. The average post-test calibration factor should not deviate from the full DGM calibration factor by more than 5%. Additional details on these procedures can be found in Method 5.

6.3.2 Temperature gauges - Each thermocouple should be permanently and uniquely marked on the casting; all mercury-in-glass reference thermometers should conform to ASTM E-1 63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at ambient air temperatures, with and without the extension lead, should be noted and recorded. Correction is necessary if the use of an extension lead produces a change greater than 1.5 percent.

6.3.2.1 Impinger, organic module, and dry gas meter thermocouples - For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2® resin bed, three-point calibration at ice-water, room-air, and boiling-water temperatures is necessary. The thermocouples should be accepted only if the readings at all three temperatures agree to ± 2°C with those of the absolute value of the reference thermometer.

6.3.2.2 Probe and stack thermocouple - For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and hot-oil-bath temperatures should be performed; it is recommended that room-air temperature be added, and that the thermometer and the thermocouple agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

6.3.3 Probe heater - The probe heating system should be calibrated prior to field use according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the curves of APTD-0576 are used.

6.3.4 Barometer - The field barometer should be adjusted initially and before each test series to agree within 2.5 mm Hg of the mercury-in-glass barometer or with the station pressure value reported by a nearby National Weather Service station, corrected for elevation. The correction for elevation difference between the station and the sampling point should be applied at a rate of -2.4 mm Hg/30 m of elevation increase. The results should be recorded on the pretest sampling check form.

6.3.5 Probe nozzle - Probe nozzles should be calibrated before initial use in the field. The ID of the nozzle should be measured with a micrometer to the nearest 0.025 mm. Three measurements should be made using different diameters each time and the average obtained. The difference between the high and the low numbers should not exceed 0.1 mm. When nozzles become damaged they should not be used again. Each nozzle should be permanently and uniquely identified.

6.3.6 Pitot tube - The Type S pitot tube assembly should be calibrated using the procedure outlined in EPA Method 2.

6.3.7 Balance - The balance should be calibrated initially by using ASTM Class 1 (Class S) standard weights and should be within 0.5 g of the standard weight.

6.4 Sampling train preparation - Care should be taken to ensure a clean sampling train preparation area free of excessive dust and organic compounds for preparing the sampling train.

6.4.1 Preparation of impingers - During preparation and assembly of the sampling train, all train openings where contamination can enter should be sealed until just prior to assembly or until sampling is about to begin.

6.4.1.1 The first impinger should be left empty (used as a water knock-out impinger due to long run times).

6.4.1.2 Approximately 100 mL of reagent water should be placed in the second and third impingers. This method does not require that organic analyses be conducted on the impinger contents. However, if analyses of semivolatile organic compounds are to be conducted, then the proper specifications on cleaning the impingers and water quality (i.e., HPLC-grade water) should be observed.

6.4.1.3 Approximately 200 to 300 g of silica gel should be placed in the fourth impinger. All impingers should be weighed separately to the nearest 0.5 g and the weights recorded. Impingers should be connected with glass U-tube connectors.

6.4.2 Filter loading - A filter should be placed in a properly-cleaned filter holder using cleaned tweezers or clean disposable surgical gloves. The filter should be properly centered and the gasket (if used) properly placed to prevent the sample gas stream from circumventing the filter. The filter should be checked for tears after the assembly is completed.

6.4.3 Sorbent loading - The XAD-2® should be loaded and sealed in the analytical (preparation) laboratory.

6.4.4 Final assembly - The final assembly of the filter holder, condenser, and sorbent module can be performed at the stack location. All components should be sealed with either precleaned foil or socket joints.

6.5 Sampling train leak check procedures - Leak checks are necessary to assure that the sample has not been biased low by dilution air. Both pre-test and post-test leak checks are necessary.

6.5.1 Pre-test - After the sampling train has been assembled, the train should be leak checked at the sampling site by plugging the nozzle and pulling a 380 mm Hg vacuum. Leakage rates greater than 4% of the average sampling rate or 0.00057 m^3/min, whichever is less, are unacceptable. Leak checks should be conducted according to Method 5 criteria.

6.5.2 During the sampling - If a component (e.g., filter assembly, sorbent module, or impinger) change is necessary during the sampling run, a leak check should be conducted before the change. The leak check should be done according to the procedure outlined above, except that it should be at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage is less than 0.00057 m^3/min or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester should record the leakage rate and either void the sampling run or perform sample volume leak corrections (if approved by the Agency). After replacing the train component, an initial leak check should be completed before sampling.

6.5.3 Post-test - The leak check should be completed at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is less than 0.00057 m^3/min or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained the tester shall either void the sample run or perform sample volume leak corrections (if approved by the Agency).

6.6 Sampling train operation

6.6.1 Final pre-test sampling checks - After conducting the initial leak check, the following checks should be made:

- Meter box examination
- Manometers leveled and zeroed
- Pump checked for proper operation
- Pitot lines leak checked
- Probe markings verified
- Thermocouples reading correctly
- Size and orientation of the nozzle verified
- Method 3 equipment for CO_2/O_2 checked for proper assembly and leak checked and
- Isokinetic K-factor checked to ensure that it is correct.

Immediately prior to sampling:

- Portholes should be cleaned to minimize the chance of sampling deposited material
- Probe and filter heating system temperatures should be checked
- Condenser/sorbent cooling system temperatures should be checked and
- Proper nozzle location should be verified.

6.6.2 The sampling procedure below should be followed.

6.6.2.1 Sampling - Initial dry gas meter readings, barometric pressure, and temperatures should be recorded. The tip of the probe should be positioned at the first sampling point with the nozzle tip pointing directly into the gas stream. When the probe is in position, the open area around the probe and the porthole should be blocked off to prevent flow disturbances and non-representative dilution of the gas stream. The pump should be turned on and the sample flow adjusted immediately to attain isokinetic conditions. The Method 3 sampling system should be turned on. Velocity pressures should be recorded and the sampling rate adjusted to isokinetic. Other readings of velocity pressure (ΔP), orifice pressure (ΔH), stack gas temperature (T_s), probe temperature (T_p), filter temperature (T_f), sorbent trap temperature (T_t), silica gel impinger temperature (T_{sg}), dry gas meter inlet and outlet temperatures (T_m), dry gas meter volume, and sample vacuum should be made.

6.6.2.2 The stack should be traversed as directed in Method 5 procedures. At each sample point, the above readings should be taken and sample flow rates adjusted to isokinetic. Following the traverses, the pump is turned off, the probe removed from the stack, and the final DGM readings recorded. Care should be taken not to bump the nozzle against stack walls in order to minimize the chance of breakage or extracting deposited material. Following each port traverse, a leak check is recommended in order to ensure a leak tight system. An additional leak check may also be performed after the train is moved to the next port, prior to sampling. The necessary post-test leak check should be conducted and the leak rate recorded.

6.6.2.3 Periodically during the test run, the connecting glassware from the probe, through the filter, and to the condenser should be checked for water condensation. If any condensation is evident, verify that the temperature sensors and heater systems are functioning properly. Ice should be maintained around the impingers to keep both the sorbent trap entrance and silica gel exit temperature at 20°C. Filter vacuum should be checked for sudden increases. The filter should be changed if the vacuum exceeds 15 in. Hg. The manometer level and zero should also be checked periodically during each traverse, because vibrations and temperature fluctuations can cause the manometer zero to shift.

6.6.2.4 Following the post-test leak check, the probe should be disconnected, and the nozzle and the end of the probe capped with precleaned aluminum foil, or equivalent caps. The inlet to the filter holder should be capped according to one of the methods previously mentioned. It may be necessary to loosen the seal between the sorbent module outlet and the inlet to the first impinger to prevent water from being drawn back into the module when the sample train cools. Alternatively, the filter holder, condenser and sorbent module may be disassembled and immediately capped at the stack location and removed to the sample recovery area.

6.7 Collection of blanks - Four different sampling blanks should be collected: field blanks, reagent blanks, proof blanks, and method blanks (laboratory only). Only two sampling blanks should be analyzed initially: the field blank and the laboratory method blank. If the field blank has high levels of contamination and the laboratory blank does not show high background levels of PCDD/PCDF, the other blanks should be analyzed to help determine the source of the contamination. Blanks are further discussed in Sec. 8.0.

7.0 PROCEDURE

7.1 Recovery preparation - Proper recovery procedure begins as soon as the probe is removed from the stack at the end of the sampling period. The nozzle end of the sampling probe should be sealed with precleaned aluminum foil and disconnected from the filter holder. When the probe is cool enough to be handled safely, all external particulate matter near the tip of the probe should be wiped off and both ends of the probe closed off with aluminum foil. Both openings to the filter holder, transfer line (if used), condenser, sorbent trap, and impinger train should be disconnected and sealed. Care should be taken not to lose any condensed water upstream of the impingers (if present) during this process.

Train components should be transferred to the cleanup area. This area should be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, is not allowed in the cleanup area. Cleanup personnel should wash their hands prior to sample recovery. The train should be inspected prior to and during disassembly and any abnormal conditions, e.g., broken filter, colored impinger liquid, etc., noted.

7.2 Sample recovery procedure - As shown in Figure 3, the sampling train should be recovered into four containers. The procedures applicable to each sample container are briefly discussed in the following section.

7.2.1 Filter (Container 1) - The filter should be removed carefully from the filter holder and placed in its identified container. Cleaned tweezers should be used to handle the filter. Fold the filter, if necessary, with the particulate cake inside the fold. Any particulate matter and filter fibers which adhere to the filter holder gasket should be transferred to the container by using a dry inert bristle brush and a sharp-edged blade. The container should be sealed with Teflon® tape.

7.2.2 Front half rinse (Container 2) - Quantitatively recover material deposited in the nozzle, probe liner, probe transfer line, cyclone (if used), and the front half of the filter holder. Brush while rinsing three times each with acetone and then rinse three times with methylene chloride. All rinses should be put into Container 2. The outside of the probe, the pitot tube, and the nozzle should be cleaned to prevent particulates from being brushed into the sample bottle. The probe liner should be tilted and rotated while squirting acetone into the upper end to assure complete wetting of the inside surface. Acetone is then squirted into the upper end while pushing the probe brush through the liner with a twisting motion, with the drainage caught in the sample bottle (Container 2). The brushing procedure should be repeated two more times or until no particles are visible in the drainage and a visual inspection of the liner reveals no particles remaining inside. The brush should be rinsed into the sample bottle to collect any particulates that may be retained within the bristles. The three acetone rinses are followed with methylene chloride and two rinses with toluene allowing the rinsate to collect into the same sample container.

After all the rinsings have been collected, the lid on the sample container should be tightened securely. As a precaution in case of leakage, the liquid level should be marked on the sample container and the cap sealed with Teflon® tape. The sample recovery should be recorded on the sample recovery form.

7.2.3 Sorbent module (Container 3) - The sorbent module should be removed from the train, tightly capped at both ends with aluminum foil or glass caps, labeled and stored on ice for transport to the laboratory. Care should be taken to ensure that no ice water can leak into the stored traps or any other train component.

7.2.4 Back half rinse (Container 4) - Rinse the back half of the filter holder, the connecting line between the filter holder and the condenser, and the condenser itself (if separate from the trap) three times with acetone, followed by two rinses with methylene chloride and two rinses with toluene. The sample container (Container 4) is then identified and sealed as discussed above.

7.2.5 Impinger water - Any color or film in the impinger water should be noted on the sample recovery form. The entrained moisture in the first three impingers should be measured to within ± 1 mL by using a graduated cylinder or by weighing to within 0.5 g by using a balance, and the data recorded appropriately. This information is needed to calculate the moisture content of the effluent gas. If the sampling train catch is to be analyzed exclusively for dioxins and furans, then the impinger liquid may be discarded after the volume or weight is recorded.

7.2.6 Silica gel - The color of the indicating silica gel should be noted on the recovery form to determine if it has been completely spent and the impinger weighed to determine entrained moisture weight gain. Analysis is not required.

7.3 Analysis summary - The following section summarizes the analytical procedures for quantitating PCDD/PCDF collected by the sampling train. Sample preparation procedures and the basic analytical techniques are listed. The detailed analytical protocol can be found in Method 8290.

7.3.1 As shown in Figure 4, the analytical procedure requires the sampling train to be analyzed in two fractions. Containers 1 and 2 (filter and front half rinse) are combined and analyzed. Containers 3 and 4 (sorbent trap and back half rinse) are also combined and analyzed. In this way filter surrogate standard recoveries and XAD-2® surrogate standard recoveries are both determined separately.

7.3.2 Acceptance criteria and corrective actions for surrogate recoveries are as follows:

7.3.2.1 All PCDD/PCDF surrogate recoveries should be within 70 to 130 percent.

7.3.2.2 If all isomer recoveries are greater than 130 percent, the sampling runs should be repeated,

7.3.2.3 If all isomer recoveries are less than 70 percent, the sampling runs should either be repeated or the final results should be divided by the fraction of surrogate recovery.

7.3.2.4 If some of the isomer recoveries are within the acceptance range and some are not, then the final results for the isomers outside the range should be divided

by the fraction of the surrogate recovery, the resulting corrected results should be flagged in the data tables, and a discussion should be included in the final report.

7.3.2.5 Acceptance criteria for other standard recoveries (i.e., internal) should conform to Method 8290 requirements.

7.3.3 As discussed in Secs. 5.1.2 and 5.2.1, surrogate spikes are added to the sorbent trap prior to sampling and to the filter immediately prior to extraction. The same set of isotopically-labeled compounds is used for these spikes. The analytical procedure for both fractions is given in the following sections. All samples should be extracted within 30 days of collection and analyzed within 45 days of extraction.

7.3.4 Sample preparation and internal standard addition - The following procedure should be performed for the filter/front half analysis and the sorbent trap/back half analysis. The only difference between the two procedures is that surrogate standards are added to the filter/front half fraction immediately prior to sample preparation whereas the surrogate standards have already been added to the sorbent trap/back half prior to sampling.

7.3.4.1 Filter/front half fraction procedures - Place a cellulose extraction thimble, 1 g of silica gel or sodium sulfate, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

7.3.4.2 Add exactly 1.0 mL of the surrogate spiking solution (Sec. 5.1.2) uniformly onto the surface of the filter while it is still in the petri dish in which it was returned from the field, using an adjustable pipet. Transfer the filter directly to the extraction thimble of the extraction system. Rinse the petri dish with 10 mL of toluene three times collecting the rinsate into the beaker.

7.3.4.3 Concentrate the sample in Container 2 (acetone/ methylene chloride rinses) to a volume of about 1-2 mL using a Kuderna-Danish concentrator apparatus, followed by nitrogen blow down at a temperature of less than 37°C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter in the Soxhlet apparatus described above.

7.3.4.4 Add 40 µL of the internal standard solution. Fortification is accomplished by using the sample fortification solutions described in Table 1. Cover the contents of the extraction thimble with the cleaned glass wool plug and proceed to the extraction procedure.

7.3.4.5 Sorbent trap/back half fraction procedures - Prepare another extraction thimble/silica gel system as described above. Suspend the adsorbent module directly over the extraction thimble in the beaker. The glass frit of the module should be in the up position. Using a Teflon® squeeze bottle containing toluene, flush the XAD-2® into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble, first with methanol, if needed, then with toluene into the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add glass wool plug from the XAD-2® sampling module to the thimble.

7.3.4.6 Concentrate the sample in Container 4 (acetone/methylene chloride rinses) to a volume of about 1 - 2 mL using a Kuderna-Danish concentrator apparatus, followed by nitrogen evaporation at a less than 37°C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. Add the concentrate to the XAD-2® resin in the Soxhlet apparatus described above.

7.3.4.7 Add 40 µL of the internal standard solution. Fortification is accomplished by using the sample fortification solutions described in Table 1. Cover the contents of the extraction thimble with a cleaned glass wool plug to prevent the XAD-2® resin from floating into the solvent reservoir of the extractor and proceed with extraction (Sec. 7.3.2).

7.3.5 Sample extraction - Place the thimble in the extractor and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately two-thirds full. Add Teflon® boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-mL between rinses to the rotary evaporator. Concentrate the extract to approximately 10 mL.

Use a nitrogen evaporative concentrator to reduce the volume of the extract to about 100 µL. Redissolve the residue in 5 mL of hexane.

7.3.6 Sample clean-up and fractionation - Sample extracts described above are spiked with 40 µL of the alternate standard fortification solution, then divided into two equal portions. One half of each sample extract is archived for future needs. The other portion is solvent-exchanged to hexane then subjected to three column chromatographic cleanup steps as described in Method 8290.

7.3.7 Analysis summary - The samples are analyzed with a high resolution gas chromatographic column coupled to a high resolution mass spectrometer (HRGC/HRMS) using the instrumental parameters described below. Prior to analysis, the Recovery Standard solution from Table 1 is added to each sample. Sample extracts are first analyzed using a capillary column to determine the concentration of each isomer of PCDDs and PCDFs (tetra- through octa-). If 2,3,7,8-TCDF is detected in this analysis, another aliquot of the sample is analyzed separately, using a second, dissimilar column to confirm and more accurately measure the 2,3,7,8-TCDF isomer. Other column systems may be used, provided that the user is able to demonstrate by means of calibration and performance checks that the column system is able to meet the specifications of Method 8290.

7.3.8 All other analytical specifications for determining the amounts of PCDD/PCDF isomers collected in the filter/front half and sorbent trap/back half fractions can be found in Method 8290.

7.4 Calculations

The mass of each isomer from the front half train fraction is added to that from the back half fraction to obtain a train total before further calculation. If a measurable amount of the isomer is found in one fraction, but the amount in the second fraction is below detection limit, the following strategy is recommended, but is subject to being overruled by regulatory authorities. Count the "nondetect" as zero if the detection limit is less than 10% of the total of the detected amount from the other fraction. In cases where the detection limit in the second fraction is greater than 10% of

the amount detected in the first fraction, then report the total as greater than the detected amount but less than the detected amount plus the second fraction detection limit.

The following section describes the calculations used to determine gas concentrations and emissions of PCDD and PCDF isomers. Toxic equivalent calculations are not included in this method. Each set of calculations should be repeated or spot-checked, as a QC measure. Calculations should be carried out to at least one extra decimal place beyond that of the acquired data and should be rounded off after final calculation to two significant digits for each run or sample. All rounding of numbers should be performed in accordance with the ASTM 380-76 procedures.

The nomenclature and sampling equations are presented in Sec. 7.4.1.

7.4.1 Sampling nomenclature

A_n = Cross sectional area of nozzle, m^2 (ft^2).

A_s = Cross sectional area of stack, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_i = Concentration of pollutant i, µg/dscm (lb/dscf).

E_i = Emission rate of pollutant i, g/sec (lb/hr).

D_N = Diameter of nozzle, mm (in.)

I = Percent of isokinetic sampling.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

M_d = Molecular weight of dry stack gas, g/g-mole (lb/lb-mole).

M_s = Molecular weight of wet stack gas, g/g-mole (lb/lb-mole).

m_i = Mass of pollutant i collected by sampling train, µg (lb).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_{static} = Static gauge pressure of stack gas, mm H_2O (in. H_2O).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{sd} = Average stack gas volumetric flow, dry, standard conditions, dscmm (dscfm).

R = Ideal gas constant, 0.06236 [(mm Hg) (m^3)] / [(°K) (g-mole)] {21.85 [(in. Hg) (ft^3)] / [(°R) (lb-mole)]}.

T_m = Absolute average DGM temperature°K (°R).

T_s = Absolute average stack gas temperature °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{lc} = Total volume liquid collected in impingers and silica gel (mL).

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

Y = Dry gas meter calibration factor.

ΔP = Average pressure differential across pitot tube, mm H_2O (in.H_2O).

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

K_p = $$85.49 \frac{ft}{sec}\left[\frac{(lb/lb-mole)\ (in.\ Hg)}{°R\ (in.\ H_20)}\right]^{1/2}$$

13.6 = Specific gravity of mercury.

7.4.2 Dry gas volume - Correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in. Hg) by using the following equation, where:

K_i = 0.3858 °K/mm Hg for metric units, or

= 17.64 °F/in. Hg for English units.

If the leak corrections to sample volume are necessary and have been approved by the test administrator, follow procedures listed in Method 0010.

7.4.3 Volume of water vapor

$$V_{w(std)} = V_{lc}\frac{\rho_w\ R\ T_{std}}{M_w\ P_{std}} = K_2\ V_{lc}$$

where:

$$K_2 = 0.001333 \text{ m}^3/\text{mL for metric units, or}$$

$$= 0.04707 \text{ ft}^3/\text{mL for English units.}$$

7.4.4 Moisture content

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas should be made, one from the impinger analysis (Sec. 7.4.3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} should be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in a "Note" in Sec. 1 of Method 4. For the purposes of this method, the average stack gas temperature may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ± 2°C.

7.4.5 Absolute stack gas pressure

$$P_s = P_{bar} + \frac{P_{static}}{13.6}$$

7.4.6 Average molecular weight of dry stack gas

$$\text{Dry: } M_d = (0.32 \times \%O_2) \times (0.44 \times \%CO_2) + (0.28 \times (100 - (\%O_2 + \%CO_2))$$

$$\text{Wet: } M_s = M_d \times (1 - B_{ws}) + (B_{ws} \times M_w)$$

7.4.7 Stack gas velocity at stack conditions

$$V_s = K_p \times C_p \times \sqrt{\Delta P} \times \sqrt{\frac{T_s + T_{std}}{P_s \times M_s}}$$

7.4.8 Average stack gas volumetric flow at dry, standard conditions

$$Q_{sd} = V_s \times A_s \times (1 - B_{ws}) \times \frac{T_{std} \times P_s}{T_s \times P_{std}} \times \frac{60 \text{ sec}}{\text{min}}$$

7.4.9 Concentration of pollutant

$$C_i = \frac{M_i}{V_{m(std)}}$$

7.4.10 Emission of pollutant

$$E_i = \frac{C_i \times Q_{sd}}{\left(60 \ \frac{sec}{min}\right)\left(1 \times 10^6 \ \frac{ug}{g}\right)}$$

7.4.11 Isokinetic sampling rate

$$\%I = \frac{1039.5746 \times V_{m(std)} \times (T_s + 460)}{V_s \times \theta \times P_s \times (1 - B_{ws}) \times (D_n)^2}$$

*English units

8.0 QUALITY CONTROL

The following quality control (QC) guidelines outline pertinent steps to be followed during the production of emission data to ensure and quantify the acceptability and reliability of the data generated.

8.1 Sampling QC procedures - Quality control procedures specific to manual source gas sampling procedures should follow EPA Method 5 and those listed in EPA Manual 600/4-77-0276 for Method 5. Sampling QC procedures are summarized in Table 2.

8.2 Blanks

8.2.1 Field blank - A field blank should be collected from a set of glassware that has not been used to collect any field samples. In the case of results exceeding regulatory limits, field blank data may be useful for convincing the regulatory official that contamination was the cause. This may result in retesting rather than a violation charge. Collection of the field blank is optional but recommended. Collect one field blank for every nine test runs at each test location.

8.2.2 Optional Glassware blank (proof blank) - A proof blank should be periodically recovered from sampling train glassware that is used to collect organic samples. The precleaned glassware, which consists of a probe liner, filter holder, condenser coil, and impinger set, is loaded as if for sampling and then quantitatively recovered exactly as the samples will be. Analysis of the generated fractions will ensure that laboratory contamination levels are under control.

8.2.3 Reagent blank - Reagent blanks should contain 500 mL of each reagent used at the test site. Reagent blanks are saved for potential analysis. Each reagent blank is part of the same lot used during the sampling program. If a field blank is unsatisfactory because of contamination, reagent blanks may be analyzed to determine the specific source of contamination. Collect one reagent blank per compliance test and archive for future analysis in the event that the field blank shows contamination.

8.2.4 Laboratory method blank - A method blank is a performance control sample that is prepared in the laboratory and processed in a manner identical to a field sample. The XAD-2® resin should be from the same batch used for preparation of the field traps. One laboratory method blank should be analyzed for every batch of samples analyzed.

9.0 METHOD PERFORMANCE

9.1 Method performance evaluation - Evaluation of analytical procedures for a selected series of compounds shall include the sample preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

9.2 Method detection limit - The overall method detection limits (lower and upper) should be calculated as shown in Sec. 6.2.3.1. Generally, analytical detection limit for tetra-CDD/CDF congeners are 50 pg. Penta-, hexa-, and hepta- congener detection limits are 250 pg and octa-congener detection limits are 500 pg.

9.3 Method precision and bias - The overall method precision and bias should be determined on a compound-by-compound basis at a given concentration level. The method precision value includes a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias is dependent upon the collection, retention, and extraction efficiency of the train components. Interlaboratory testing of Method 0023 and Method 8290 to establish method accuracy and precision for sampling a variety of stationary sources has not been performed.

10.0 REFERENCES

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12. Rom, J.J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. U.S. Environmental Protection Agency, Research Triangle Park, NC. Air Pollution Technical Document (APTD) 0576, March 1972.

TABLE 1

COMPOSITION OF THE SAMPLE FORTIFICATION
AND RECOVERY STANDARDS SOLUTIONS

Analyte	Method 0023 Concentration (pg/µL)	Method 8290 Concentration[1] (pg/µL)
Internal Standards		
$^{13}C_{12}$-2,3,7,8-TCDD	100	10
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	10
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	25
$^{13}C_{12}$-OCDD	100	50
$^{13}C_{12}$-2,3,7,8-TCDF	100	10
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	10
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	25
Surrogate Standards		
$^{37}Cl_4$-2,3,7,8-TCDD	100	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	
Recovery Standards		
$^{13}C_{12}$-1,2,3,4-TCDD	500	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500	50
Alternate Standard		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	--

[1] Provided as reference only; also see Method 8290.

TABLE 2

SAMPLING QC PROCEDURES SUMMARY

QC Procedure	Frequency	Criteria
Sample equipment calibrations	See Sec. 6.3.1	See Sec. 6.3.1
Dry gas meter sample leak check	Before and after each test run	0.00057 cmm ($\leq$ 0.02 cfm) or 4% of sample rate whichever is less at highest vacuum
O_2 and CO_2 sampling system leak check	Once per test	See Method 3, or equivalent for Method 3A
ΔP meter leveling	Before and after each test run	Level
Pitot tube leak check	Before and after each test run	No visible leak observed at 75 mm (3 in.) H_2O for 15 seconds
Pitot tube orientation check	Every test	Pitot tube is level with no visible rotation from perpendicular to flow
Cyclonic flow check	Made at every location	$< 20^\circ$ average offset from perpendicular to flow
Probe, filter, trap, and silica gel impinger are maintained at specified temperature ranges	Every test	See Sec. 4.0
Overall isokinetic sampling rate	Every test	± 10% of 100%
Sampling blanks	See Sec. 8.2	See Sec. 8.2

TABLE 3

REQUIREMENTS FOR ANALYTICAL PREPARATION,
SURROGATE RECOVERIES AND SAMPLE BLANKS

Item	Description	Control Limit
Precleaning filters	Soxhlet extraction	Detection limits listed in Sec. 9.2
Precleaning sorbent	Soxhlet extraction	Detection limits listed in Sec. 9.2
Filter and sorbent surrogate spikes	Isotopically-labeled compounds	70 to 130% recovery
Field blank	Collect one for every 9 sample runs at each test location	< 5 times the detection limits
Method blank	Prepared at analytical laboratory (laboratory blank). One per analytical batch	Criteria decided by laboratory QA officer
Reagent blanks	One per lot of solvent used. Archive for possible analysis	Analyze only if requested by Agency to determine source of field blank confirmation
Proof Blank	One per set of glassware. Archive for possible analysis (collect only if requested by Agency)	Analyze only if requested by Agency to determine source of field blank contamination

TABLE 4

SAMPLE EQUIPMENT CALIBRATION SUMMARY

Equipment	Procedure	Frequency	Control Limits
Primary WTM[a] or DGM[a]	Primary calibration	Every 12 months	± 1% average
Sample DGM	Full calibration	Every 6 months	$Y_i \leq 2\%$ from Y_{avg}
Sample DGM	Post calibration	After each test program	$Y_{post} \leq 5\%$ from Y_{full}
Thermometers, Thermocouples	Calibration check	Initially	± 2°C (3.6°F) at 3 point calibration from reference thermometer
Nozzle	ID calibration	Before every test program	Repeated measurements ± 0.1 mm (0.004 in.)
Pitot tube	Wind tunnel calibration or construction specifications verification	Before every test program	Specifications listed in Method 2
ΔP gauge (if not an inclined manometer)	See Method 2	Once/test program	Within 5% of reference at three readings
Balance	Calibration check	Initially	Observed weight ≤ 0.5 g from Class S weight
Barometer	Calibration check	Initially	< 0.1 in. Hg from primary barometer

[a]WTM = wet test meter; DGM = dry gas meter.

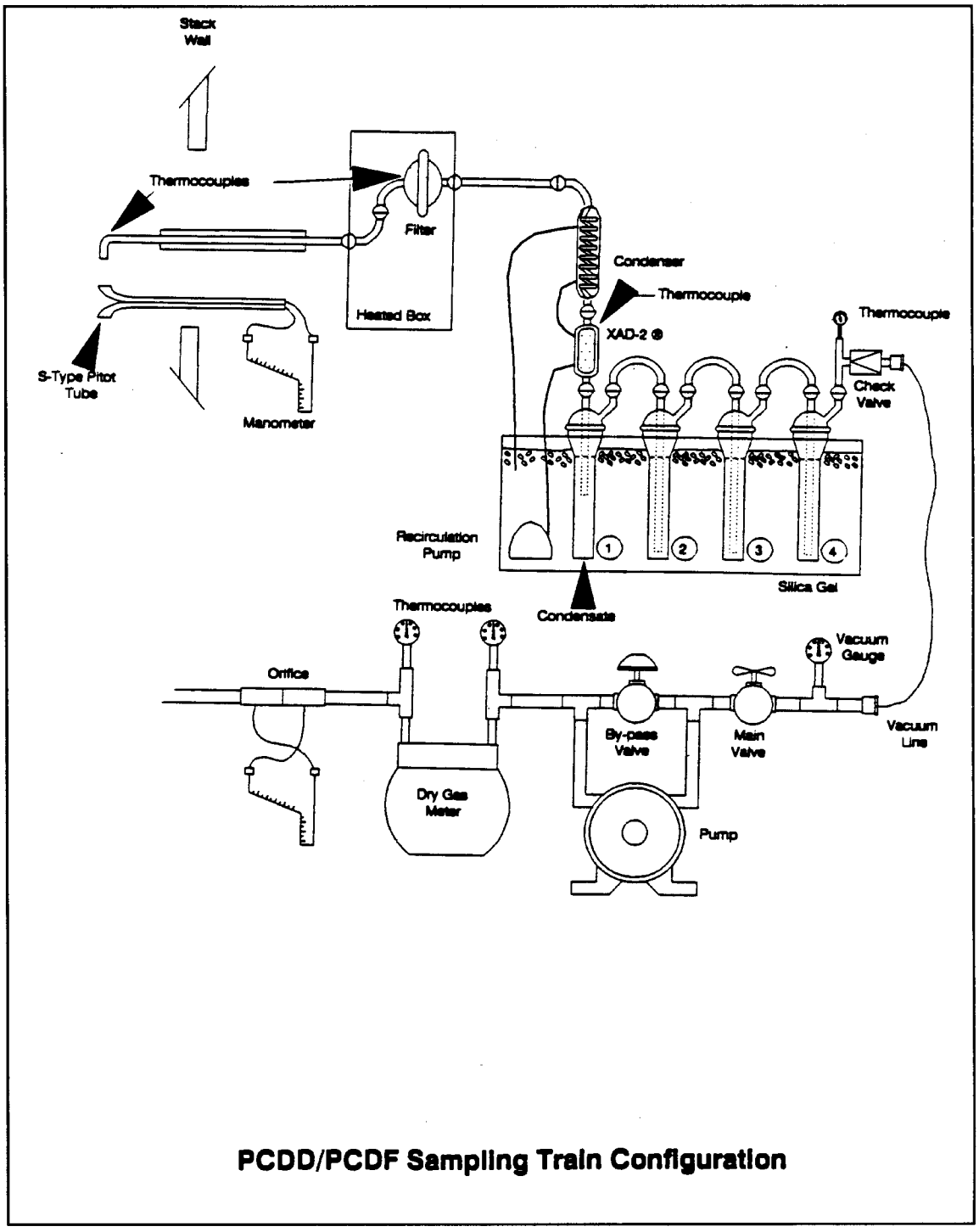
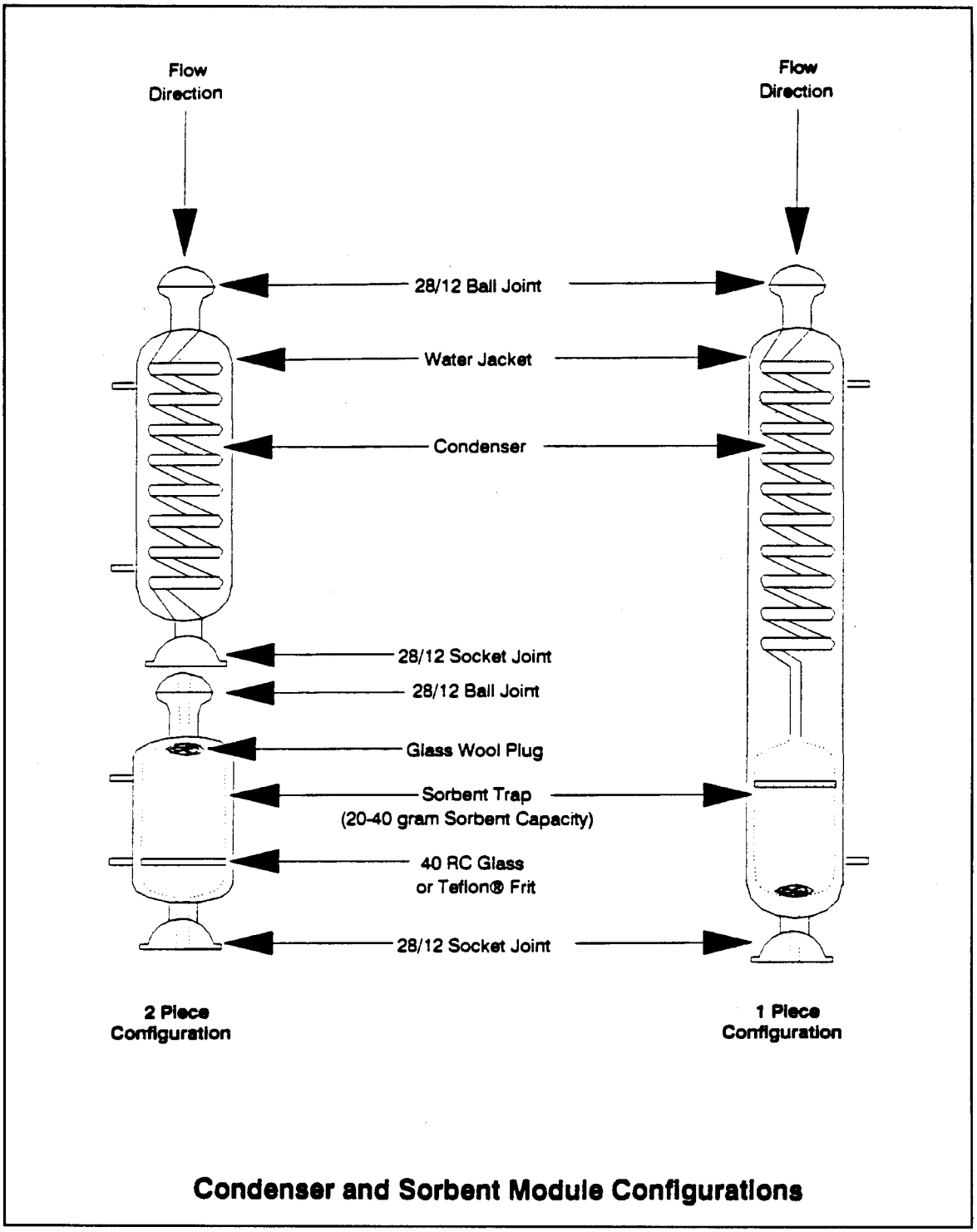
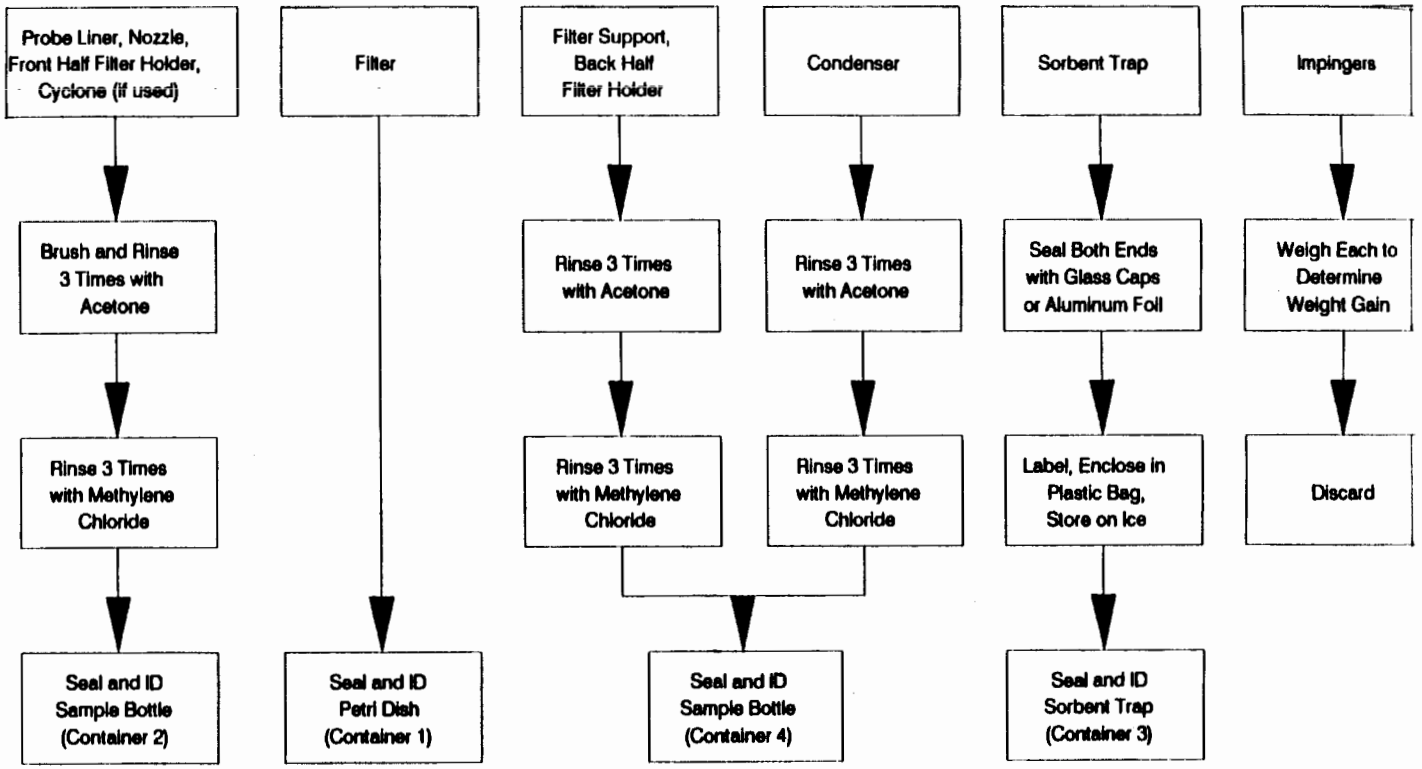

Stack Wall
Thermocouples
Filter
Heated Box
Condenser
Thermocouple
XAD-2 ®
Thermocouple
Check Valve
S-Type Pitot Tube
Manometer
Recirculation Pump
1
2
3
4
Silica Gel
Condensate
Thermocouples
Vacuum Gauge
Orifice
By-pass Valve
Main Valve
Vacuum Line
Dry Gas Meter
Pump
PCDD/PCDF Sampling Train Configuration

Figure 1



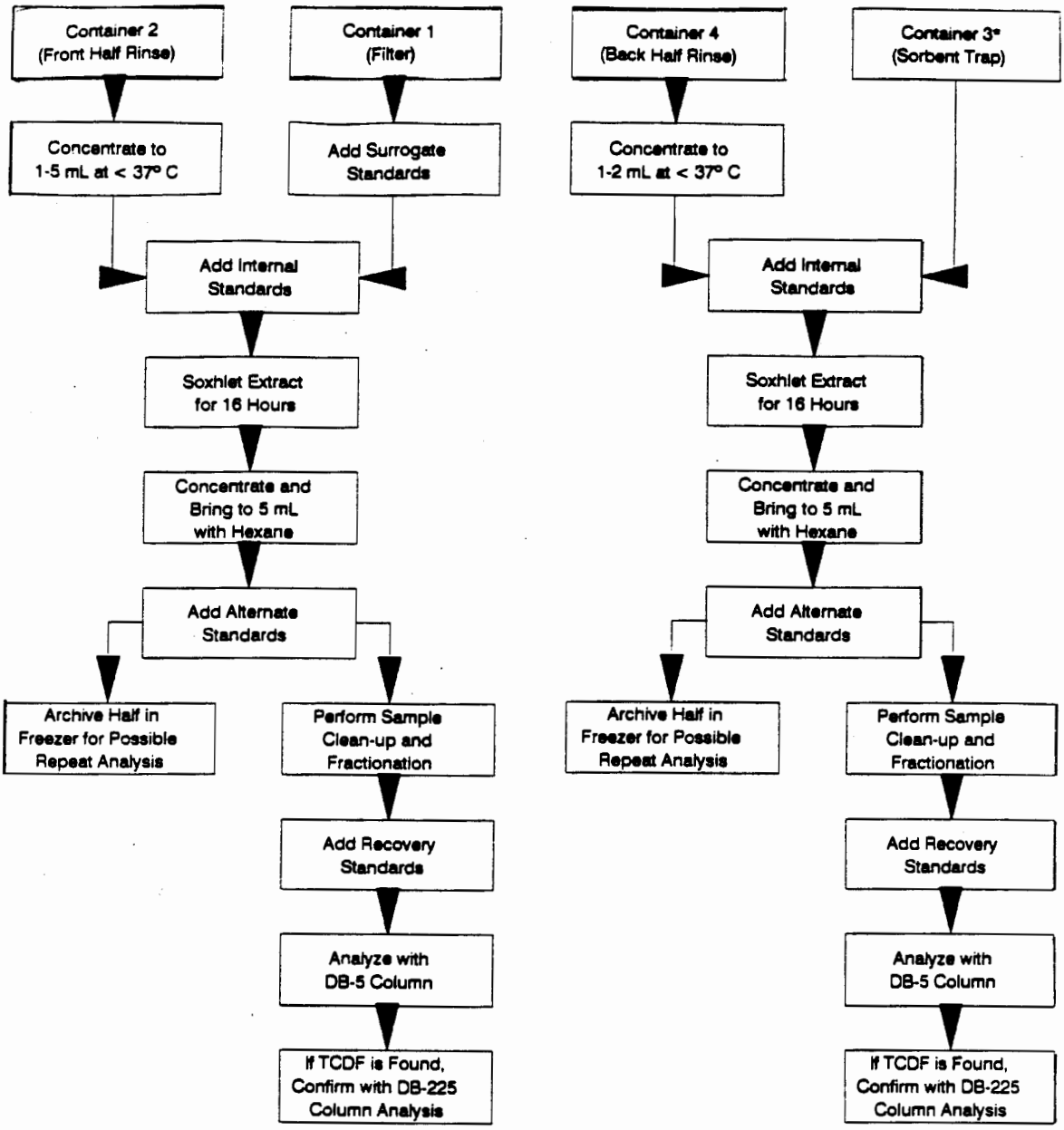
Condenser and Sorbent Module Configurations

Figure 2



PCDD/PCDF Sample Recovery Scheme

FIGURE 4



* Surrogate Standards are added to the sorbent trap prior to sampling

PCDD/PCDF Analytical Summary Scheme

APPENDIX A
RECOMMENDED AUDITING PROCEDURES

An audit is an independent assessment of data quality. Both performance audits and system audits may be performed.

Performance Audit - A performance audit is conducted to evaluate quantitatively the quality of data produced by the sampling, analysis, or the total measurement system (sample collection, sample recovery, sample analysis, and data processing).

Audit Sample - A performance audit sample contains tetra- through octa-isomers of PCDD and PCDF. Audit samples are not normally required.

Performance Audit of the Field Test - A field test performance audit may be conducted by checking the dry gas meter for accuracy using procedures located in the Quality Assurance Handbook for Air Pollution Measurement Systems (EPA 600/4-77-027b). Performance audits on thermocouple readings, ΔP gauges, barometric pressure gauges and others, may also be conducted.

Performance Audit of Data Processing - The data processing procedures may be audited by requiring the testing laboratory to provide an example calculation for one sample run. This example calculation will include all the calculations used to determine the emissions based on the raw field and laboratory data.

System Audit - A system audit is an on-site, qualitative inspection and review of the total measurement system.

The functions of the auditor are:

a) Observe procedures and techniques of the field team during sample collection and sample recovery; and

b) Examine records of apparatus calibrations and other quality control procedures used in sampling and analytical activities

When on-site, the auditor observes the source test team's overall performance, including the following operations:

a) Setting the sampling system and leak checking the sample train and pitot tube;

b) Collecting the samples isokinetically;

c) Conducting the final leak checks; and

d) Sample documentation procedures, sample recovery, and preparation of the samples for shipment.

METHOD 0030

VOLATILE ORGANIC SAMPLING TRAIN

1.0 PRINCIPLE AND APPLICATION

1.1 Principle

1.1.1 This method describes the collection of volatile principal organic hazardous constituents (POHCs) from the stack gas effluents of hazardous waste incinerators. For the purpose of definition, volatile POHCs are those POHCs with boiling points less than 100°C. If the boiling point of a POHC of interest is less than 30°C, the POHC may break through the sorbent under the conditions of the sample collection procedure.

1.1.2 Field application for POHCs of this type should be supported by laboratory data which demonstrate the efficiency of a volatile organic sampling train (VOST) to collect POHCs with boiling points less than 30°C. This may require using reduced sample volumes collected at flow rates between 250 and 500 mL/min. Many compounds which boil above 100°C (e.g., chlorobenzene) may also be efficiently collected and analyzed using this method. VOST collection efficiency for these compounds should be demonstrated, where necessary, by laboratory data of the type described above.

1.1.3 This method employs a 20-liter sample of effluent gas containing volatile POHCs which is withdrawn from a gaseous effluent source at a flow rate of 1 L/min, using a glass-lined probe and a volatile organic sampling train (VOST). (Operation of the VOST under these conditions has been called FAST-VOST.) The gas stream is cooled to 20°C by passage through a water-cooled condenser and volatile POHCs are collected on a pair of sorbent resin traps. Liquid condensate is collected in an impinger placed between the two resin traps. The first resin trap (front trap) contains approximately 1.6 g Tenax and the second trap (back trap) contains approximately 1 g each of Tenax and petroleum-based charcoal (SKC Lot 104 or equivalent), 3:1 by volume. A total of six pairs of sorbent traps may be used to collect volatile POHCs from the effluent gas stream.

1.1.4 An alternative set of conditions for sample collection has been used. This method involves collecting sample volume of 20 liters or less at reduced flow rate. (Operation of the VOST under these conditions has been referred to as SLO-VOST.) This method has been used to collect 5 liters of sample (0.25 L/min for 20 min) or 20 liters of sample (0.5 L/min for 40 min) on each pair of sorbent cartridges. Smaller sample volumes collected at lower flow rates should be considered when the boiling points of the POHCs of interest are below 35°C. A total of six pairs of sorbent traps may be used to collect volatile POHCs from the effluent gas stream.

1.1.5 Analysis of the traps is carried out by thermal desorption purge-and-trap by gas chromatography/mass spectrometry (see Method 5040). The VOST is designed to be operated at 1 L/min with traps being replaced every 20 min for a total sampling time of 2 hr. Traps may be analyzed separately or combined onto one trap to improve detection limit. However, additional flow rates and sampling times are acceptable. Recent experience has shown that when less than maximum detection ability is required, it is acceptable and probably preferable to operate the VOST at 0.5 L/min for a total of three 40-min periods. This preserves the 2-hr sampling period, but reduces the number of cartridge changes in the field as well as the number of analyses required.

1.2 Application

1.2.1 This method is applicable to the determination of volatile POHCs in the stack gas effluent of hazardous waste incinerators. This method is designed for use in calculating destruction and removal efficiency (DRE) for the volatile POHCs and to enable a determination that DRE values for removal of the volatile POHCs are equal to or greater than 99.99%.

1.2.2 The sensitivity of this method is dependent upon the level of interferences in the sample and the presence of detectable levels of volatile POHCs in blanks. The target detection limit of this method is 0.1 ug/m^3 (ng/L) of flue gas, to permit calculation of a DRE equal to or greater than 99.99% for volatile POHCs which may be present in the waste stream at 100 ppm. The upper end of the range of applicability of this method is limited by breakthrough of the volatile POHCs on the sorbent traps used to collect the sample. Laboratory development data have demonstrated a range of 0.1 to 100 ug/m^3 (ng/L) for selected volatile POHCs collected on a pair of sorbent traps using a total sample volume of 20 liters or less (see Paragraph 1.1.4).

1.2.3 This method is recommended for use only by experienced sampling personnel and analytical chemists or under close supervision by such qualified persons.

1.2.4 Interferences arise primarily from background contamination of sorbent traps prior to or after use in sample collection. Many potential interferences can be due to exposure of the sorbent materials to solvent vapors prior to assembly and exposure to significant concentrations of volatile POHCs in the ambient air at hazardous waste incinerator sites.

1.2.5 To avoid or minimize the low-level contamination of train components with volatile POHCs, care should be taken to avoid contact of all interior surface or train components with synthetic organic materials (e.g., organic solvents, lubricating and sealing greases), and train components should be carefully cleaned and conditioned according to the procedures described in this protocol.

2.0 APPARATUS

2.1 Volatile Organic Sampling Train: A schematic diagram of the principal components of the VOST is shown in Figure 1 and a diagram of one acceptable version of the VOST is shown in Figure 2. The VOST consists of a glass-lined probe followed by an isolation valve, a water-cooled glass condenser, a sorbent cartridge containing Tenax (1.6 g), an empty impinger for condensate removal, a second water-cooled glass condenser, a second sorbent cartridge containing Tenax and petroleum-based charcoal (3:1 by volume; approximately 1 g of each), a silica gel drying tube, a calibrated rotameter, a sampling pump, and a dry gas meter. The gas pressure during sampling and for leak-checking is monitored by pressure gauges which are in line and downstream of the silica gel drying tube. The components of the sampling train are described below.

2.1.1 **Probe:** The probe should be made of stainless steel with a borosilicate or quartz glass liner. The temperature of the probe is to be maintained above 130°C but low enough to ensure a resin temperature of 20°C. A water-cooled probe may be required at elevated stack temperatures to protect the probe and meet the above requirements. Isokinetic sample collection is not a requirement for the use of VOST since the compounds of interest are in the vapor phase at the point of sample collection.

2.1.2 **Isolation valve:** The isolation valve should be a greaseless stopcock with a glass bore and sliding Teflon plug with Teflon wipers (Ace 8193 or equivalent).

2.1.3 **Condensers:** The condensers (Ace 5979-14 or equivalent) should be of sufficient capacity to cool the gas stream to 20°C or less prior to passage through the first sorbent cartridge. The top connection of the condenser should be able to form a leak-free, vacuum-tight seal without using sealing greases.

2.1.4 **Sorbent cartridges:**

2.1.4.1 The sorbent cartridges used for the VOST may be used in either of two configurations: the inside-outside (I/O) configuration in which the cartridge is held within an outer glass tube and in a metal carrier, and the inside-inside (I/I) configuration in which only a single glass tube is used, with or without a metal carrier. In either case, the sorbent packing will be the same.

2.1.4.1.1 The first of a pair of sorbent cartridges shall be packed with approximately 1.6 g Tenax GC resin and the second cartridge of a pair shall be packed with Tenax GC and petroleum-based charcoal (3:1 by volume; approximately 1 g of each).

2.1.4.1.2 The second sorbent cartridge shall be packed so that the sample gas stream passes through the Tenax layer first and then through the charcoal layer.

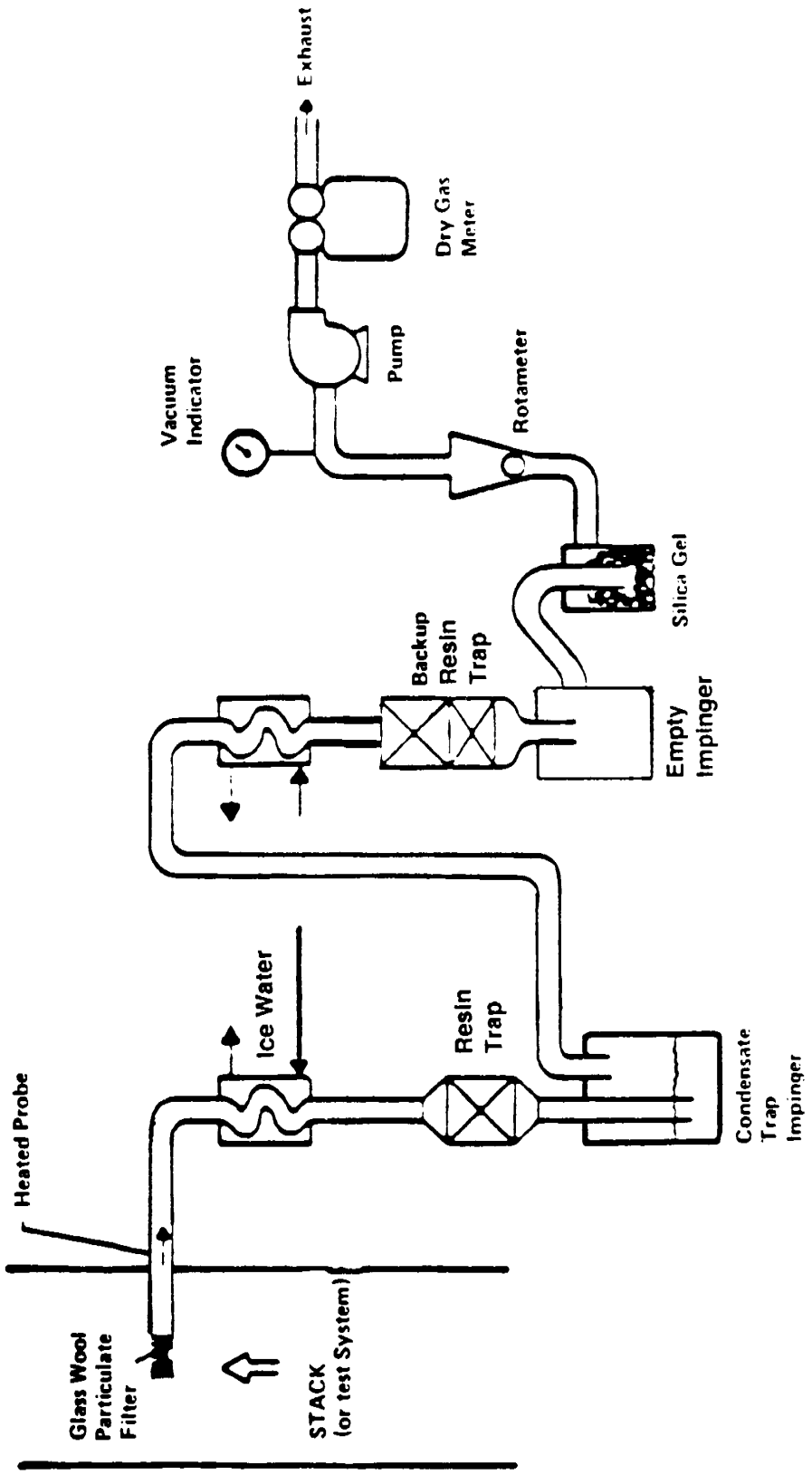


Figure 1. Schematic of Volatile Organic Sampling Train (VOST).

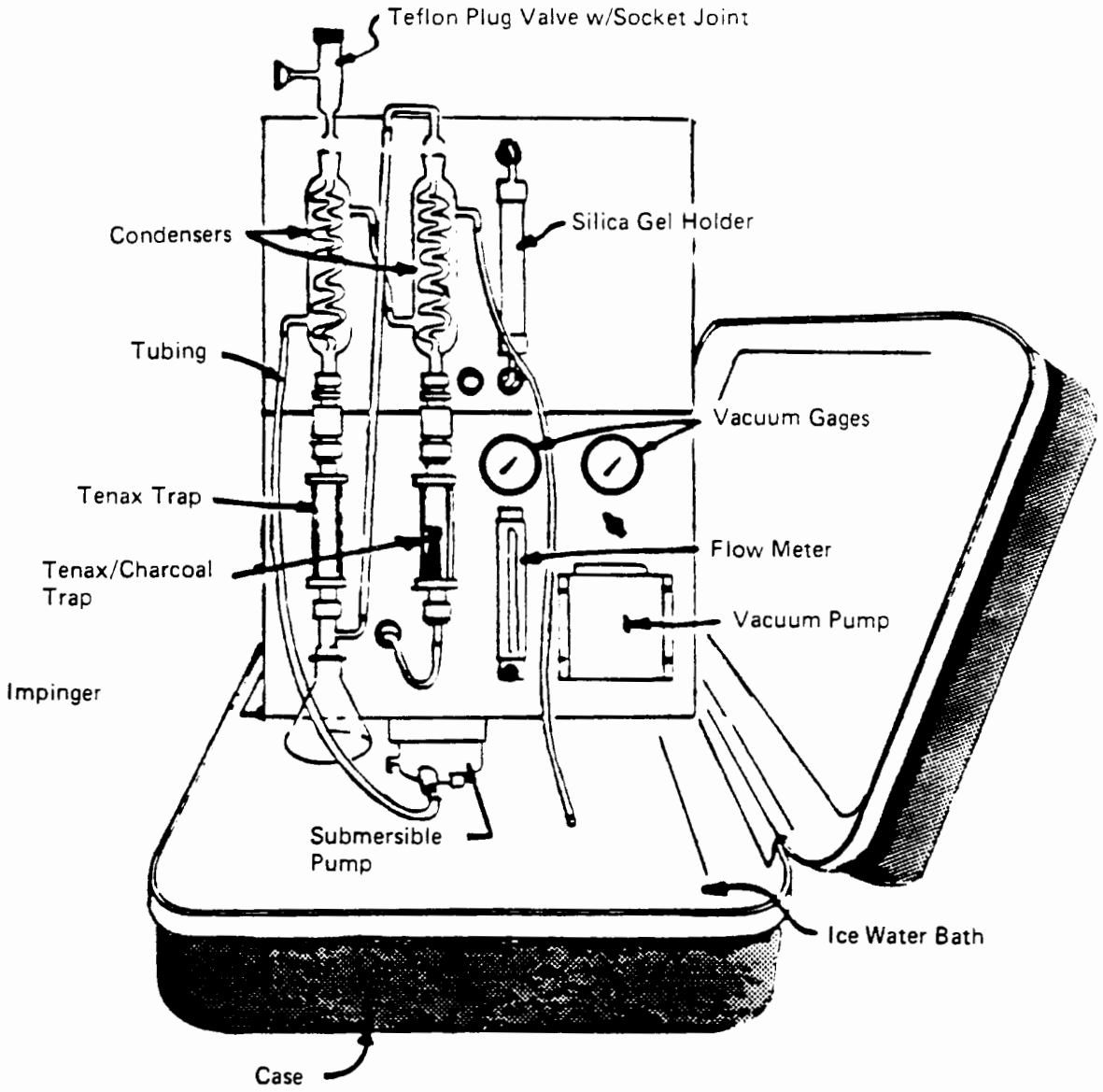


Figure 2. Volatile Organic Sampling Train (VOST).

2.1.4.2 The sorbent cartridges shall be glass tubes with approximate dimensions of 10 cm by 1.6 cm I.D. The two acceptable designs (I/O, I/I) for the sorbent cartridge are described in further detail below.

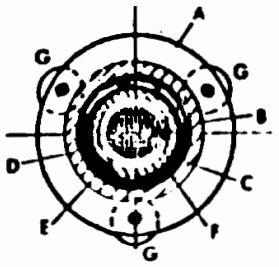
2.1.4.2.1 **Inside/Inside sorbent cartridge:** A diagram of an I/I sorbent cartridge is shown in Figure 3. This cartridge is a single glass tube (10 cm by 1.6 cm I.D.) which has the ends reduced in size to accommodate a 1/4- or 3/8-in. Swagelok or Cajon gas fitting. The resin is held in place by glass wool at each end of the resin layer. The amounts of each type of sorbent material used in the I/I design are the same as for the I/O design. Threaded end caps are placed on the sorbent cartridge after packing with sorbent to protect the sorbent from contamination during storage and transport.

2.1.4.2.2 **Inside/Outside type sorbent cartridge:** A diagram of an I/O sorbent cartridge is shown in Figure 4. In this design the sorbent materials are held in the glass tube with a fine mesh stainless steel screen and a C-clip. The glass tube is then placed within a larger diameter glass tube and held in place using Viton O-rings. The purpose of the outer glass tube is to protect the exterior of the resin-containing tube from contamination. The two glass tubes are held in a stainless steel cartridge holder, where the ends of the glass tubes are held in place by Viton O-rings placed in machine grooves in each metal end piece. The three cylindrical rods are secured in one of the metal end pieces and fastened to the other end piece using knurled nuts, thus sealing the glass tubes into the cartridge holder. The end pieces are fitted with a threaded nut onto which a threaded end cap is fitted with a Viton O-ring seal, to protect the resin from contamination during transport and storage.

2.1.5 **Metering system:** The metering system for VOST shall consist of vacuum gauges, a leak-free pump (Thomas Model 107 or equivalent, Thomas Industries, Sheboygan, Wisconsin), a calibrated rotameter (Linde Model 150, Linde Division of Union Carbide, Keasbey, New Jersey) for monitoring the gas flow rate, a dry gas meter with 2% accuracy at the required sampling rate, and related valves and equipment. Provisions should be made for monitoring the temperature of the sample gas stream between the first condenser and first sorbent cartridge. This can be done by placing a thermocouple on the exterior glass surface of the outlet from the first condenser. The temperature at that point should be less than 20°C. If it is not, an alternative condenser providing the required cooling capacity must be used.

2.1.6 **Sample transfer lines:** All sample transfer lines to connect the probe to the VOST shall be less than 5 ft in length, and shall be heat-traced Teflon with connecting fittings which are capable of forming leak-free, vacuum-tight connections without the use of sealing grease.

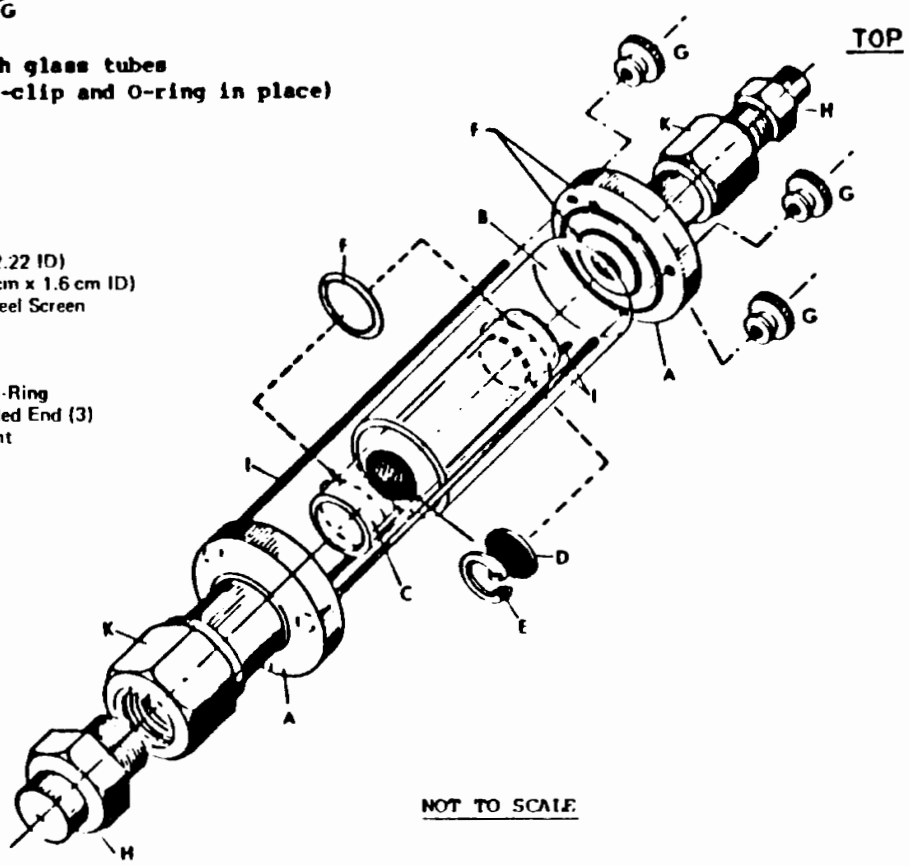
Figure 3. Inside-inside vost cartridge



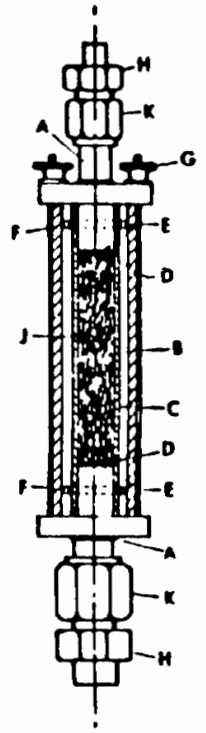
Section cut through glass tubes
(showing screen, C-clip and O-ring in place)

LEGEND

A - Stainless Steel Carrier
B - Glass Tube (9.84 L x 2.22 ID)
C - Small Glass Tube (10 cm x 1.6 cm ID)
D - Fine Mesh Stainless Steel Screen
E - Stainless Steel C-Clip
F - O-Ring (Viton)
G - Nuts (4)
H - End Cap with Viton O-Ring
I - Metal Rod with Threaded End (3)
J - Tenax/Charcoal Sorbent
K - Cajon Fitting



NOT TO SCALE



Assembled Trap
NTS

Figure 4. Sorbent Trap Assembly (I/O)
Volatile Organic Sampling Train (VOST)

All other sample transfer lines used with the VOST shall be Teflon with connecting fittings that are capable of forming leak-free, vacuum-tight connections without the use of sealing grease.

3.0 REAGENTS AND MATERIALS

3.1 2,6-Diphenylene oxide polymer (Tenax, 35/60 mesh):

3.1.1 The new Tenax is Soxhlet extracted for 24 hr with methanol (Burdick & Jackson, pesticide grade or equivalent). The Tenax is dried for 6 hr in a vacuum oven at 50°C before use. Users of I/O and I/I sorbent cartridges have used slightly different thermal conditioning procedures. I/O sorbent cartridges packed with Tenax are thermally conditioned by flowing organic-free nitrogen (30 mL/min) through the resin while heating to 190°C. Some users have extracted new Tenax and charcoal with pentane to remove nonpolar impurities. However, these users have experienced problems with residual pentane in the sorbents during analysis.

3.1.2 If very high concentrations of volatile POHCs have been collected on the resin (e.g., micrograms of analytes), the sorbent may require Soxhlet extraction as described above. Previously used Tenax cartridges are thermally reconditioned by the method described above.

3.2 Charcoal (SKC petroleum-base or equivalent): New charcoal is prepared and charcoal is reconditioned as described in Paragraph 4.4. New charcoal does not require treatment prior to assembly into sorbent cartridges. Users of VOST have restricted the types of charcoal used in sorbent cartridges to only petroleum-based types. Criteria for other types of charcoal are acceptable if recovery of POHC in laboratory evaluations meet the criteria of 50 to 150%.

3.3 Viton-O-Ring: All O-rings used in VOST shall be Viton. Prior to use, these O-rings should be thermally conditioned at 200°C for 48 hr.
O-rings should be stored in clean, screw-capped glass containers prior to use.

3.4 Glass tubes/Condensers: The glass resin tubes and condensers should be cleaned with a nonionic detergent in an ultrasonic bath, rinsed well with organic-free water, and dried at 110°C. Resin tubes of the I/O design should be assembled prior to storage as described in Paragraph 4.1. Resin tubes of the I/I design can be stored in glass culture tube containers with cotton cushioning and Teflon-lined screw caps. Condensers can be capped with appropriate end caps prior to use.

3.5 Metal parts: The stainless steel carriers, C-clips, end plugs, and screens used in the I/O VOST design are cleaned by ultrasonication in a warm nonionic detergent solution, rinsed with distilled water, air-dried, and heated in a muffle furnace for 2 hr at 400°C. Resin tubes of the I/I design require Swagelok or equivalent end caps with Supelco M-1 ferrules. These should be heated at 190°C along with the assembled cartridges.

3.6 Silica gel (Indicating type, 6-16 mesh): New silica gel may be used as received. Silica gel which has been previously used should be dried for 2 hr at 175°C (350°F).

3.7 Cold packs: Any commercially available reusable liquids or gels that can be repeatedly frozen are acceptable. They are typically sold in plastic containers as "Blue Ice" or "Ice-Packs." Enough should be used to keep cartridges at or near 4°C.

3.8 Water: Water used for cooling train components in the field may be tap water; and water used for rinsing glassware should be organic-free.

3.9 Glass wool: Glass wool should be Soxhlet extracted for 8 to 16 hr, using methanol, and oven dried at 110°C before use.

4.0 SAMPLE HANDLING AND PROCEDURE

4.1 Assembly:

4.1.1 The assembly and packing of the sorbent cartridges should be carried out in an area free of volatile organic material, preferably a laboratory in which no organic solvents are handled or stored and in which the laboratory air is charcoal filtered. Alternatively, the assembly procedures can be conducted in a glove box which can be purged with organic-free nitrogen.

4.2 Tenax cartridges:

4.2.1 The Tenax, glass tubes, and metal cartridge parts are cleaned and stored (see Section 3.0). Approximately 1.6 g of Tenax is weighed and packed into the sorbent tube which has a stainless steel screen and C-clip (I/O design) or glass wool (I/I design) in the downstream end. The Tenax is held in place by inserting a stainless steel screen and C-clips in the upstream end (I/O design) or glass wool (I/I design). Each cartridge should be marked, using an engraving tool, with an arrow to indicate the direction of sample flow, and a serial number.

4.2.2 Conditioned resin tubes of the I/O design are then assembled into the metal carriers according to the previously described inside/inside or inside/outside procedures (with end caps) and are placed on cold packs for storage and transport. Conditioned resin tubes of the I/I design are capped and placed on cold packs for storage and transport.

4.3 Tenax/Charcoal tubes

4.3.1 The Tenax, charcoal, and metal cartridge parts are cleaned and stored as previously described (see Section 3.0). The tubes are packed with approximately a 3:1 volume ratio of Tenax and charcoal (approximately 1 g each). The Tenax and charcoal are held in place by the stainless steel screens and C-clips (I/O design) or by glass wool (I/I design). The glass tubes containing the Tenax and charcoal are then

conditioned as described below (see Paragraph 4.4). Place the I/O glass tubes in the metal carriers (see Paragraph 2.1.4.2.2), put end caps on the assembled cartridges, mark direction of sample flow and serial number, and place the assembled cartridges on cold packs for storage and transport.

4.3.2 Glass tubes of the I/I design are conditioned, and stored in the same manner as the I/O tubes.

4.4 Trap Conditioning - QC

4.4.1 Following assembly and leak-checking, the traps are connected in reverse direction to sampling to a source of organic-free nitrogen, and nitrogen is passed through each trap at a flow rate of 40 mL/min, while the traps are heated to 190°C for 12-28 hr. The actual conditioning period may be determined based on adequacy of the resulting blank checks.

4.4.2 The following procedure is used to blank check each set of sampling cartridges prior to sampling to ensure cleanliness. The procedure provides semi-quantitative data for organic compounds with boiling points below 110°C on Tenax and Tenax/Charcoal cartridges. It is not intended as a substitute for Method 5040.

4.4.2.1 The procedure is based on thermal desorption of each set of two cartridges, cryofocusing with liquid nitrogen onto a trap packed with glass beads, followed by thermal desorption from the trap and analysis by GC/FID.

4.4.2.2 The detection limit is based on the analysis of Tenax cartridges spiked with benzene and toluene and is around 2 ng for each compound.

4.4.2.3 The results of analyzing spiked cartridges on a daily basis should not vary by more than 20 percent. If the results are outside this range, the analytical system must be evaluated for the probable cause and a second spiked cartridge analyzed.

4.4.2.4 The GC operating conditions are as follows:

GC Operating Conditions

Column: Packed column 6 ft x 1/8" stainless steel 1.0 percent SP-1000 on Carbopack B 60/80, or equivalent.
Temperature program: 50°C for 5 min, 20°C/min increase to 190°C, hold 13 min.
Injector: 200°C.
Detector: F.I.D. 250°C.
Carrier Gas: Helium at 25 mL/min.
Sample valve: Valco 6-port with 40" x 1/16" stainless steel trap packed with 60/80 mesh glass beads.
Cryogen: Liquid nitrogen.
Trap heater: Boiling water, hot oil, or electrically heated.

Desorption heater: Supelco "clam shell" (high capacity carrier gas purifier) heater and Variac, adjusted to 180°C to 200°C.

4.4.2.5 Calibration is accomplished by preparing a spiked Tenax cartridge with benzene and toluene and analyzing according to the standard operating procedure. A standard of benzene, toluene and bromofluorobenzene (BFB) is prepared by injecting 2.0 uL of benzene and toluene and 1.0 uL of BFB into 10 mL of methanol. The concentration of this stock is 175 ng/uL of benzene and toluene, and 150 ng/uL BFB. One microliter of the stock standard is injected onto a Tenax cartridge through a heated injection port set at 150°C. A GC oven can be used for this with the oven at room temperature. Helium carrier gas is set at 50 mL/min. The solvent flush technique should be used. After two min, remove the Tenax cartridge and place in the desorption heater for analysis. BFB is also used as an internal standard spike for GC/MS analysis which provides a good comparison between GC/FID and GC/MS. The results of this spike analysis should not vary more than 20 percent day to day. Initially and then periodically this spiked Tenax should be reanalyzed a second time to verify that the 10 min desorption time and 180-200°C temperature are adequate to remove all of the spiked components. It should be noted that only one spiked Tenax cartridge need be prepared and analyzed daily unless otherwise needed to ensure proper instrument operation.

An acceptable blank level is left to the discretion of the method analyst. An acceptable level is one that allows adequate determination of expected components emitted from the waste being burned.

4.4.3 After conditioning, traps are sealed and placed on cold packs until sampling is accomplished. Conditioned traps should be held for a minimum amount of time to prevent the possibility of contamination.

4.4.4 It may be useful to spike the Tenax and Tenax/charcoal traps with the compounds of interest to ensure that they can be thermally desorbed under laboratory conditions. After spiked traps are analyzed they may be reconditioned and packed for sampling.

4.5 Pretest preparation:

4.5.1 All train components shall be cleaned and assembled as previously described. A dry gas meter shall have been calibrated within 30 days prior to use, using an EPA-supplied standard orifice.

4.5.2 The VOST is assembled according to the schematic diagram in Figure 1. The cartridges should be positioned so that sample flow is

through the Tenax first and then the Tenax/charcoal. Cooling water should be circulated to the condensers and the temperature of the cooling water should be maintained near 0°C. The end caps of the sorbent cartridges should be placed in a clean screw-capped glass container during sample collection.

4.6 Leak-checking:

4.6.1 The train is leak-checked by closing the valve at the inlet to the first condenser and pulling a vacuum of 250 mm (10 in. Hg) above the normal operating pressure. The traps and condensers are isolated from the pump and the leak rate noted. The leak rate should be less than 2.5 mm Hg after 1 min. The train is then returned to atmospheric pressure by attaching a charcoal-filled tube to the train inlet and admitting ambient air filtered through the charcoal. This procedure will minimize contamination of the VOST components by excessive exposure to the fugitive emissions at hazardous waste incinerator sites.

4.7 Sample Collection

4.7.1 After leak-checking, sample collection is accomplished by opening the valve at the inlet to the first condenser, turning on the pump, and sampling at a rate of 1 liter/min for 20 min. The volume of sample for any pair of traps should not exceed 20 liters.

4.7.2 Following collection of 20 liters of sample, the train is leak-checked a second time at the highest pressure drop encountered during the run to minimize the chance of vacuum desorption of organics from the Tenax. The train is returned to atmospheric pressure, using the method discussed in Paragraph 4.1 and the two sorbent cartridges are removed. The end caps are replaced and the cartridges shall be placed in a suitable environment for storage and transport until analysis. The sample is considered invalid if the leak test does not meet specification.

4.7.3 A new pair of cartridges is placed in the VOST, the VOST leak-checked, and the sample collection process repeated as described above. Sample collection continues until six pairs of traps have been used.

4.7.4 All sample cartridges should be kept on cold packs until they are ready for analysis.

4.8 Blanks

4.8.1 **Field blanks/trip blanks:** Blank Tenax and Tenax/charcoal cartridges are taken to the sampling site and the end caps removed for the period of time required to exchange two pairs of traps on VOST. After the two VOST traps have been exchanged, the end caps are replaced on the blank Tenax and Tenax/charcoal tubes and these are returned to the cold packs and analyzed with the sample traps. At least one pair of field blanks (one Tenax, one Tenax/charcoal) shall be included with each

six pairs of sample cartridges collected (or for each field trial using VOST to collect volatile POHCs).

4.8.2 **Trip blanks:** At least one pair of blank cartridges (one Tenax, one Tenax/charcoal) shall be included with shipment of cartridges to a hazardous waste incinerator site. These "field blanks" will be treated like any other cartridges except that the end caps will not be removed during storage at the site. This pair of traps will be analyzed to monitor potential contamination which may occur during storage and shipment.

4.8.3 **Laboratory blanks:** One pair of blank cartridges (one Tenax, one Tenax/charcoal) will remain in the laboratory using the method of storage which is used for field samples. If the field and trip blanks contain high concentrations of contaminants (e.g., greater than 2 ng of a particular POHC), the laboratory blank shall be analyzed in order to identify the source of contamination.

5.0 CALCULATIONS (for sample volume)

5.1 The following nomenclature are used in the calculation of sample volume:

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm (in.) Hg.

P_{std} = Standard absolute pressure, 760 mm (29.92 in.) Hg.

T_m = Dry gas meter average absolute temperature, K (°R).

T_{std} = Standard absolute temperature, 293K (528°R).

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).

γ = Dry gas meter calibration factor.

5.2 The volume of gas sampled is calculated as follows:

$$V_{m(std)} = V_m \gamma \frac{T_{std}\ P_{bar}}{T_m\ P_{std}} = K_1 \gamma \frac{V_m\ P_{bar}}{T_m}$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or

K_1 = 17.64 °R/in. Hg for English units.

6.0 ANALYTICAL PROCEDURE

See Method 5040.

7.0 PRECISION AND ACCURACY REQUIREMENTS

7.1 Method Performance Check

Prior to field operation of the VOST at a hazardous waste incinerator, a method performance check should be conducted using either selected volatile POHCs of interest or two or more of the volatile POHCs for which data are available. This check may be conducted on the entire system (VOST/GC/MS) by analysis of a gas cylinder containing POHCs of interest or on only the analytical system by spiking of the POHCs onto the traps. The results of this check for replicate pairs of traps should demonstrate that recovery of the analytes fall within 50% to 150% of the expected values.

7.2 Performance Audit

During a trial burn a performance audit must be completed. The audit results should agree within 50% to 150% of the expected value for each specific target compound. This audit consists of collecting a gas sample containing one or more POHCs in the VOST from an EPA ppb gas cylinder. Collection of the audit sample in the VOST may be conducted either in the laboratory or at the trial burn site. Anaysis of the VOST audit sample must be by the same person, at the same time, and with the same analytical procedure as used for the regular VOST trail burn samples. EPA ppb gas cylinders currently available for VOST Audit are shown in Table 1 below.

The audit procedure, audit equipment and audit cylinder may be obtained by writing:

Audit Cylinder Gas Coordinator (MD-77B)
Quality Assurance Division
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

or by calling the Audit Cylinder Gas Coordinator at (919) 541-4531.

The request for the audit must be made at least 30 days prior to the scheduled trial burn. If a POHC is selected for which EPA does not have an audit cylinder, this audit is not required.

8.0 REFERENCES

1. Protocol for the Collection and Analysis of Volatile POHCs Using VOST. EPA/600/8-84/007, March 1984.

2. Sykes, A.L., Standard Operating Procedure for Blanking Tenax and Tenax/Charcoal Sampling Cartridges for Volatile Organic Sampling Train (VOST), Radion Corporation, P.O. Box 13000, Research Triangle Park, NC 27709.

3. Validation of the Volatile Organic Sampling Train (VOST) Protocol, Vols. I and II, EPA/600/4-86/014a, January 1986.

TABLE 1: Organic Gases in the ppb Audit Repository

Group I	Ranges of cylinders currently available:
5 Organics in N_2:	7 - 90 ppb
Carbon tetrachloride	90 - 430 ppb
Chloroform	430 - 10,000 ppb
Perchloroethylene	
Vinyl chloride	
Benzene	

Group II	Ranges of cylinders currently available:
9 Organics in N_2	7 - 90 ppb
Trichloroethylene	90 - 430 ppb
1,2-Dichloroethane	
1,2-Dibromoethane	
F-12	
F-11	
Bromomethane	
Methyl ethyl ketone	
1,1,1-Trichloroethane	
Acetronitrile	

TABLE 1: Organic Gases in the ppb Audit Repository (Continued)

Group III	Ranges of cylinders currently available:
7 Organics in N_2:	7 - 90 ppb
Vinylidene chloride	90 - 430 ppb
F-113	
F-114	
Acetone	
1,4-Dioxane	
Toluene	
Chlorobenzene	

Group IV	Ranges of cylinders currently available:
6 Organics in N_2:	7 - 90 ppb
Acrylonitrile	430 - 10,000
1,3-Butadiene	
Ethylene oxide	
Methylene chloride	
Propylene oxide	
Ortho-xylene	

SAMPLING METHOD FOR VOLATILE ORGANIC COMPOUNDS (SMVOC)

1.0 SCOPE AND APPLICATION

1.1 Method 0031 is used to determine volatile organic compounds in gaseous emissions from a wide variety of stationary sources including hazardous waste incinerators. The following compounds may be determined by this method:

Compound	Boiling Point (°C)	CAS No.[a]
Acrylonitrile[b]	77	107-13-1
Benzene	80	71-43-2
Bromodichloromethane	87	75-27-4
Carbon disulfide	46	75-15-0
Carbon tetrachloride	77	56-23-5
Chlorodibromomethane	119-120 @ 748 mm Hg	124-48-1
Chloroform	61	67-66-3
Chloroprene[c]	59	126-99-8
Dibromomethane	97	74-95-3
1,1-Dichloroethane	57	75-34-3
1,2-Dichloroethane	83	107-06-2
1,1-Dichloroethene	32	75-35-4
trans-1,2-Dichloroethene	48	156-60-5
1,2-Dichloropropane	96	78-87-5
1,3-Dichloropropene	106 @ 730 mm Hg	542-75-6
Methylene chloride	39	75-09-2
Tetrachloroethene	121	127-18-4
Toluene	111	108-88-3
1,1,1-Trichloroethane	75	71-55-6
1,1,2-Trichloroethane	113	79-00-5
Trichloroethene	87	79-01-6
Trichlorofluoromethane	24	75-69-4

[a] Chemical Abstract Services Registry Number.
[b] The water solubility and reactivity of this compound may cause problems with some stationary sources.
[c] Reactive compound; may interact with the test matrix.

1.2 Method 0031 may be used to prepare volatile organic compounds that have a boiling point between -15°C and 121°C. Field application for volatile organic compounds with boiling points less than 0°C should be supported by data obtained from laboratory gaseous dynamic spiking and gas chromatographic/mass spectrometric (GC/MS) analysis according to Methods 5041 and 8260 to demonstrate the efficiency of the sampling and analysis method.

1.3 The method is not applicable to particulates or aerosols since isokinetic sampling is not performed. Isokinetic sampling is not required because the volatile organic compounds are in the gas phase when they are sampled.

1.4 Application of Method 0031 is not restricted to those compounds in the target analyte list, however, detection limits have been determined for these compounds and acceptable method performance data have been obtained. Method 0031 may also be applied to the compounds listed in Table 1 if extra care is taken because of the high volatility of these compounds.

1.5 Method 0031 is generally not applicable to polar water-soluble and reactive volatile organic compounds. Examples of polar water-soluble and reactive compounds are shown in Table 2. Other examples where Method 0030 (VOST) sampling and analytical methodology has been used inappropriately include: bromoform (boiling point 137°C, above the maximum limit allowed by the methodology), ethylbenzene (136°C), 1,2,3-trichloropropane (156°C), xylenes (~140°C), styrene (146°C), 1,1,2,2-tetrachloroethane (146°C at 746 mm Hg), and the dichlorobenzenes (~175°C). Although successful analysis for these compounds can be demonstrated by spiking sorbent tubes, the compounds will not be collected quantitatively at the upper temperature limit for the operation of the SMVOC train.

1.6 This method is applicable to the determination of volatile organic compounds in the gaseous effluent of stationary sources such as hazardous waste incinerators with an upper concentration limit per compound in the emissions of approximately 1.5 parts per million (ppm). Method 0031 is not appropriate for gaseous volatile organic compound concentrations above this limit, since saturation of the analytical system or compound breakthrough in the field may occur. Modifications of analytical methods to reduce the concentration of compounds entering the gas chromatograph/mass spectrometer (GC/MS), such as splitters or dilutions, may prevent saturation of the analytical system, but the analytical data are not accurate if breakthrough has occurred during sampling. The analysis of screening samples or distributive volume samples is recommended to prevent analytical system saturation when high analyte concentrations may be encountered.

1.7 The sensitivity of this method is dependent upon the level of interferences in the sample matrix and the presence of detectable levels of volatile organic compounds in the blanks. The target detection limit of this method is 0.1 $\mu g/m^3$ (ng/L) of gaseous effluent. The upper end of the range of applicability of this method is limited by breakthrough of the volatile organic compounds on the sorbent traps used to collect the sample and the ability of the analytical system to respond within the linear range of the instrumentation. Laboratory method development data have demonstrated a range of 0.1 to 100 $\mu g/m^3$ (ng/L) for selected volatile organic compounds collected on a set of sorbent traps using a total sample volume of 20 L or less (see Sec. 2.3).

1.8 The SMVOC is designed to be operated at a sampling rate of 1 L/min with traps being replaced every 20 min for a total sampling time of 2 hrs. Analysis of the traps is carried out by thermal desorption purge-and-trap gas chromatography/mass spectrometry (see Methods 5041 and 8260). Traps may be analyzed separately or combined onto one trap to improve detection limits. Additional flow rates and sampling times are acceptable. For example, when less than maximum detection ability is needed, it is acceptable to operate the SMVOC at 0.5 L/min for a total of three 40-minute periods (two-hour total sampling time). In this example, a two-hour sampling time is maintained, but the number of sampling tubes which must be changed in the field is minimized, as is the number of analyses which must be performed.

NOTE: The SMVOC sampling train may be operated no slower than 0.25 L/min, and no faster than 1 L/min.

1.9 This method is restricted to use by, or under close supervision of, trained analytical personnel experienced in sampling volatile organic compounds in air. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method employs a sampling module and meter box to withdraw a 20-L sample of effluent gas containing volatile organic compounds from a stationary source at a flow rate of 1 L/min, using a glass-lined probe heated to 130 ± 5°C and a sampling method for volatile organic compounds (SMVOC) train.

2.2 The gas stream is cooled to 20°C by passage through a water-cooled condenser and volatile organic compounds are collected on a set of sorbent traps (Tenax®-GC/Tenax®-GC/Anasorb®-747). Liquid condensate is collected in an impinger placed between the two Tenax®-GC traps and the Anasorb®-747 trap. The first and second traps contain 1.6 g of Tenax®-GC each and the third trap (back trap) contains 5.0 g of Anasorb®-747. A total number of sorbent tube sets to encompass a total sampling time of 2 hrs is collected: i.e., if a sampling rate of 1 L/min for 20 minutes is used, a total of six sorbent tube sets will be collected in 2 hr of sampling.

2.3 Alternative conditions for sample collection may be used, collecting a sample volume of 20 L or less at a flow rate reduced from 1 L/min. (Operation of the SMVOC under these conditions is referred to as SLO-SMVOC.) The SLO-SMVOC may be used to collect 5 L of sample (0.25 mL/min for 20 min) or 20 L of sample (0.5 L/min for 40 min) on each set of sorbent tubes. These smaller sample volumes collected at lower flow rates should be considered when the boiling points of the volatile organic compounds of interest are below 0°C (see Table 1) to prevent breakthrough. Refer to Sec. 2.2 for the total number of tube sets collected per run.

3.0 INTERFERENCES

3.1 Interferences are encountered in the analytical methodology and arise primarily from background contamination of sorbent traps prior to or after sample collection. Other interferences may arise from exposure of the sorbent materials to solvent vapors prior to assembly and exposure to significant concentrations of volatile organic compounds in the ambient air at a stationary source site. To avoid or minimize the low-level contamination of train components with volatile organic compounds, care should be taken to avoid contact of all interior surfaces or train components with synthetic organic materials such as organic solvents, and lubricating and sealing greases. Train components should be carefully cleaned and conditioned according to the procedures described in this protocol. The use of a sealed/enclosed sampling train is suggested but not required (for example, a purged glove bag may be used). The use of blanks (Sec. 6.6) is essential to assess the extent of any contamination. Refer to Method 5041 for additional information on analytical interferences.

3.2 If the emission source has a high level of organic compounds in the emissions matrix (for example, hydrocarbons present at levels of hundreds of ppm), the presence of these volatile organic compounds may interfere with the performance of the SMVOC analytical methodology. If the probability of saturation of the analytical instrumentation exists, preliminary SMVOC screening samples with distributive volumes may be necessary to help ensure that valid and usable data will be obtained. To perform sampling according to distributive volumes, samples of different volumes are collected (typically 5 L, 10 L, and 20 L) to verify that analyte concentrations are 1X, 2X, and 4X.

4.0 APPARATUS AND MATERIALS

4.1 Sampling train - A schematic of the principal components of the SMVOC is shown in Figure 1. The SMVOC consists of a heated glass-lined probe, followed by an isolation valve and charcoal trap, a water-cooled glass condenser, two sorbent tubes containing Tenax®-GC (1.6 ± 0.1 g each), an empty knock-out trap for condensate removal, a second water-cooled glass condenser, a third sorbent tube containing Anasorb®-747 (5.0 g ± 0.1 g), a silica gel drying tube, a calibrated rotameter, a sampling pump, and a dry gas meter. The vacuum during sampling and for leak-checking is monitored by pressure gauges which are in-line with and downstream from the silica gel drying tube. The components of the sampling train are described below.

4.1.1 Probe - The probe is made of stainless steel with a borosilicate or quartz glass liner. The temperature of the probe is maintained at 130°C ± 5°C or higher, but not so high that the sorbent temperature exceeds 20°C. A water-cooled probe may be necessary at elevated source temperatures to protect the probe and meet the required sorbent temperature maximum. Isokinetic sample collection is not a requirement for the use of SMVOC since the compounds of interest are in the vapor phase at the point of sample collection. No nozzle is required, but a plug of clean quartz wool (approximately 2.5 cm. (1 in.)) is inserted in the probe to remove particulate matter.

NOTE: No stainless steel components should be in contact with the sample stream.

4.1.2 Isolation valve - The isolation valve is a greaseless stopcock (0.25 in. outer diameter stem is recommended) with a glass bore and sliding Teflon® plug with Teflon® washers (Ace Glass 8193 or equivalent).

4.1.3 Condensers - The condensers (Ace Glass 5979-14 or equivalent) must be of sufficient capacity to cool the gas stream to 20°C or less prior to passage through the first sorbent tube. The top connection of the condenser must form a leak-free, vacuum-tight seal without using sealing greases. Solverall® tube fittings and screw caps with Solverall® washers (¼ in. OD, or equivalent) are recommended.

4.1.4 Sorbent tubes - See Figure 2 for a diagram of a SMVOC tube.

4.1.4.1 The first and second tubes of a three-tube set of sorbent tubes should each be packed with 1.6 ± 0.1 g of Tenax®-GC resin and the third tube of the set should be packed with 5.0 ± 0.1 g of Anasorb®-747. The tubes should be marked with an arrow to indicate the direction of flow during sampling.

4.1.4.2 The sorbent tubes are glass tubes with approximate dimensions of 10 cm x 1.6 cm ID. The tube is a single glass tube which has the ends reduced in size to accommodate a ¼-in. Swagelok® fitting. The sorbent is held in place by unsilanized clean glass wool at each end of the sorbent layer. Threaded end caps are placed on the sorbent tube after packing with sorbent to protect the sorbent from contamination during storage and transport. In order to minimize tube breakage, fittings are finger-tight plus an additional quarter of a turn. Ceramic-filled Teflon® ferrules (Supeltex M2A or equivalent) are used for tubes. Graphite ferrules (Supeltex M4 or equivalent) are used if reconditioning of the tubes is necessary. The Swagelok® end caps should be finger-tightened with the ferrules in place so that the entire cap assembly may be turned as a unit. In order to seal the assembly and avoid glass breakage, the cap assembly should be pushed to the end of the glass and then backed off slightly before tightening

the cap with a wrench one quarter of a turn. Backing the cap assembly off from the end of the tube will prevent chipping, cracking, or breaking of the glass.

4.1.4.3 The sorbent tubes are placed in transport tubes (capped culture tubes with glass wool and charcoal) for shipment. A layer of clean charcoal is placed in the bottom of the transport tube to absorb any volatile organics in the air in the transport tube. A plug of cleaned glass wool (approximately 2.5 cm. (1 in.)) is placed above the charcoal. The SMVOC tube, with both ends capped, is placed in the transport tube, and a plug of cleaned glass wool (approximately 2.5 cm. (1 in.)) is placed on top of the SMVOC tube. The two glass wool plugs cushion the SMVOC tube during shipping. The transport tube is then sealed tightly with a Teflon®-lined screw cap. At no time, should the samples contained in the sorbent tubes be exposed to large pressure differentials such as might be caused by shipping in unpressurized aircraft cargo compartments.

4.1.5 Metering system - The metering system for SMVOC consists of a vacuum gauge, a pump, a calibrated rotameter for monitoring the sampling flow rate, a dry gas meter (2% accuracy, with a minimum resolution of 0.01 L) at the required sampling rate, needle valves, and a temperature readout device. Provisions should be made for monitoring the temperature of the sample gas stream between the first condenser and the first sorbent tube, since this temperature should not exceed 20°C. The temperature can be monitored by placing a thermocouple on the exterior glass surface of the outlet from the first condenser. The temperature at that point should be less than 20°C. If the cooling is not sufficient, an alternative condenser providing the necessary cooling capacity must be used.

4.1.6 Sample transfer lines - All sample transfer lines connecting the probe to the SMVOC shall be less than 1.52 m. (5 ft.) in length. All sample transfer lines ahead of the first condenser shall be heat-traced Teflon® or glass maintained at 130 ± 5°C. Connecting fittings must be capable of forming leak-free, vacuum-tight connections without the use of sealing grease. All other sample transfer lines used with the SMVOC shall be Teflon® with connecting fittings that are capable of forming leak-free, vacuum-tight connections without the use of sealing grease. These sample transfer lines should not be reused at other emission sources.

4.2 Solverall® washers - All washers or gaskets used in SMVOC shall be Teflon®-coated (Solverall® washers or equivalent; ¼ in. stainless steel Swagelok® fittings with Supeltex M2A ferrules may also be used). Prior to use, these gaskets should be ultrasonically-cleaned with methanol and air-dried in a contained/isolated organic vapor-free area. Gaskets should be stored in clean, screw-capped containers prior to use.

4.3 Glass wool - Glass wool shall be Soxhlet-extracted for 8 to 16 hours using methanol, and oven dried at 110°C before use. Glass wool should not be silanized to prevent contamination of samples with siloxanes. Quartz wool is recommended for high temperature applications.

4.4 Cold packs/ice - Ice or any commercially-available reusable liquids or gels that can be frozen repeatedly are acceptable. These reusable liquids are typically sold in plastic containers as "Blue Ice" or "Ice-Packs". Enough cold packs or ice should be used to maintain tubes less than 10°C. If ice is used as a coolant for the tubes, the tubes should be shielded from direct contact with the ice so they will not become wet when the ice melts. Use of dry ice (solid CO_2) for cooling tubes should be avoided; the sorbent tubes take up carbon dioxide as the solid coolant vaporizes and the analytical system is vented when the tubes are desorbed and analyzed. The tubes should not be stored at freezing temperatures, since the seal between the glass and Teflon® fittings will be compromised and diffusion of volatile organic compounds into the sorbent may occur.

4.5 VOA vials - 40-mL glass vials with Teflon®-lined screw caps are required for recovery of condensate.

4.6 Teflon® squeeze bottles -Teflon® squeeze bottles should be washed with a solution of a laboratory detergent, rinsed with hot tap water, then with distilled water, then rinsed with clean purged water prior to use.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. It is recommended that blanks be taken of all reagents used in testing.

5.2 2,6-Diphenyl-p-phenylene oxide polymer (Tenax®-GC, 35/60 mesh, or equivalent).

5.2.1 New Tenax®-GC is Soxhlet-extracted for 24 hours with methanol. The Tenax®-GC is dried for 6 hours in a vacuum oven at 50°C before use. Thermal conditioning (Sec. 7.1.1) of the Tenax®-GC should be done prior to blanking.

5.2.2 If reuse of Tenax®-GC is necessary, the polymer may be extracted sequentially with methanol and pentane, dried in a vacuum oven, and thermally reconditioned as described above. However, reused tubes must meet the same criteria for cleanliness as new tubes. Reuse of sorbents is not recommended. Common practice in laboratories where SMVOC tubes are prepared commercially or where SMVOC sampling and analysis are done extensively is not to reuse sorbents.

5.3 Anasorb®-747 - New Anasorb®-747 is used as it is received from the manufacturer without preparation other than thermal conditioning pending a Quality Control check (Sec. 7.1.1). Anasorb®-747 must not be reused. The Anasorb®-747 should not be extracted with organic solvent prior to use as a sorbent in the SMVOC.

5.4 Silica gel - Indicating type, 6-16 mesh. New silica gel may be used as received from the vendor. Silica gel should not be reused for SMVOC.

5.5 Methanol, CH_3OH - The methanol used for extracting the Tenax®-GC and glass wool should be pesticide grade or equivalent.

5.6 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 SMVOC glassware cleaning- All glass components of the train should be cleaned thoroughly. The following procedure has been found to be effective, but any protocol which consistently results in contamination-free glassware is acceptable.

6.1.1 Sonicate for 1 hour in a solution of a laboratory detergent such as Alconox®.

6.1.2 Rinse with copious amounts of hot tap water to remove all detergent residue.

6.1.3 Rinse three times with HPLC grade water.

6.1.4 Oven dry at 110°C.

6.1.5 Cap for shipment using Teflon® tape or aluminum foil.

6.2 Assembly

The assembly and packing of the sorbent tubes should be carried out in an area free of volatile organic material, such as a laboratory in which no organic solvents are handled or stored and in which the laboratory air is charcoal filtered. Alternatively, an air-tight sealed glove box is suggested.

6.3 Tenax®-GC tubes

6.3.1 The Tenax®-GC glass tubes and metal tube parts are cleaned and stored (see Sec. 6.1). Ferrules are discarded but the metal unions are cleaned by sonication in methanol. Tenax®-GC (1.6 ± 0.1 g) is weighed and packed into each of the first two sorbent tubes which have unsilanized cleaned glass wool in the downstream end. The Tenax®-GC is held in place by inserting unsilanized cleaned glass wool. Each tube should be marked, using an engraving tool, permanent marker or diamond-tipped pencil, with an arrow to indicate the direction of sample flow during sampling, and a serial number.

6.3.2 Conditioned sorbent tubes are capped and placed on cold packs or ice for storage and transport. The temperature of the tubes during storage and transport is maintained at a temperature of less than 10°C. Conditioned tubes should be held for no more than 14 days before sampling, to prevent the possibility of contamination. At no time, should the samples contained in the sorbent tubes be exposed to large pressure differentials such as might be caused by shipping in unpressurized aircraft cargo compartments.

6.4 Anasorb®-747 tubes - Anasorb®-747 (5.0 ± 0.1 g) is weighed and packed into the third sorbent tube which also has unsilanized cleaned glass wool in the downstream end. The Anasorb®-747 is held in place by inserting unsilanized cleaned glass wool. Special care should be taken to conspicuously mark the Anasorb®-747 tube with an arrow to indicate the direction of flow during sampling, and a serial number.

6.5 Sample collection

6.5.1 For sample collection, place the inlet of the probe at the centroid of the stack or at a point no closer to the walls than 1 meter. After leak checking (see Sec. 6.5.3) but before the initiation of sample collection, the probe shall be purged with stack gas. This purge can be accomplished by attaching a pump to the isolation valve upstream of the first condenser and drawing stack gas through the probe via the isolation valve, so that the probe is purged of ambient air at the initiation of sample collection.

6.5.2 Sample collection is accomplished by opening the valve at the inlet to the first condenser (see Figure 1), turning on the pump, and sampling at a rate of 1 L/min (or slower rate, if desired, according to the guidelines for SLO-SMVOC) for 20 minutes (or an appropriately longer period, if slower sampling rates are used). The volume of sample for any

set of traps should not exceed 20 liters. The end caps of the sorbent tubes should be placed in a clean screw-capped glass container during sample collection to prevent contamination.

6.5.3 Following completion of sample collection, the SMVOC is leak-checked a second time at the highest vacuum encountered during the sampling run to minimize the chance of vacuum desorption of volatile organic compounds from Tenax®-GC. The sample is considered invalid if the leak test does not meet specifications. The train is returned to atmospheric pressure and the set of sorbent tubes is removed. The end caps are replaced and the tubes are placed in an organic-free environment and maintained at a temperature less than 10°C for storage and transport. The set of tubes and any condensate collected (see Sec. 6.5.4) are placed in self-sealing plastic storage bags.

In the laboratory, tubes are maintained in a clean, organic vapor-free environment at a temperature less than 10°C until analysis. The maximum storage time between sampling and analysis of the tubes should be 14 days. The rate of loss of sorbed volatile organic compounds from the tubes is both compound-specific and source-specific. A 14-day period is chosen for the holding time before analysis to provide a reasonably conservative guideline for quantitative analysis of the volatile organic compounds which have been sampled.

NOTE: To prevent breakage and/or loosening of the seals at the end of the tubes, SMVOC tubes should not be stored in a freezer or over dry ice. A solvent-free refrigerator (no cooler than 4°C) is appropriate for storage of the tubes until analysis.

6.5.4 Depending upon condensate volume collected, recovery may be performed with each tube change, or at the end of each run (nominally 2 hrs). Collection of a single composite sample for the run may be especially appropriate when minimal condensate is being collected. If not all the sorbent tubes are analyzed, the total amount of analyte in the composite condensate should be added to the total amount for the run. The condensate is recovered by transferring any liquid contained in the knock-out trap to a 40-mL VOA vial and rinsing the knock-out trap three times with a minimum volume of organic-free reagent water (Sec. 5.6) and adding the rinses to the VOA vial. If necessary, water should be added to eliminate headspace in the vial. If there is sufficient condensate to fill more than one vial, two vials should be used. The VOA vials containing the condensate are placed, with the set of tubes, in a self-sealing plastic storage bag and maintained at a temperature less than 10°C for storage and transport until analysis. The condensate is analyzed by Method 8260. Refer to Method 8260 for details on analytical procedures. Condensate samples, like the sorbent tubes, must be analyzed within 14 days.

6.5.5 A new set of tubes is placed in the SMVOC, the SMVOC is leak-checked, and the sample collection process repeated as described above. To avoid removing the probe from the stack, it is sufficient to perform a glassware leak check using the three way valve just downstream of the probe. Sample collection continues until sufficient samples to encompass a two-hour sampling period have been collected. If samples are taken at a sampling rate of 1 L/minute, a two hour sampling period will result in the collection of six sets of tubes. If SLO-SMVOC procedures are used, fewer than six sets of tubes will be sampled over a two-hour period.

6.6 Blanks

6.6.1 Field blanks - Blank Tenax®-GC and Anasorb®-747 tubes are attached to the sampling train while the train is leak-checked. The tubes are removed and stored with the sample tubes. At least one field blank should be collected for every two-hour sampling period.

6.6.2 Trip blanks - At least one set of blank tubes (two Tenax®-GC, one Anasorb®-747) should be included with each shipment of tubes to a stationary source sampling site. These trip blanks should be treated like any other tubes except that the end caps will not be removed during storage at the site. This set of tubes should be analyzed to assess contamination which may occur during storage and shipment.

6.6.3 Laboratory blanks - One set of blank tubes (two Tenax®-GC, one Anasorb®-747) should remain in the laboratory using the method of storage which is used for field samples. These laboratory blanks should be from the same batch of sorbent as used for the field blanks, trip blanks and collected samples. If the field and trip blanks contain high concentrations of contaminants (e.g., greater than 2 ng of a particular volatile organic compound), the laboratory blank should be analyzed in order to identify the source of contamination.

7.0 PROCEDURE

7.1 Tube conditioning

7.1.1 In a desorption oven, the sorbent tubes are connected to a source of organic-free nitrogen. Nitrogen is passed through each tube at a flow rate of 80-100 mL/min while the tubes are heated. Anasorb®-747 is thermally conditioned for 18-24 hours at 300°C, under a nitrogen flow rate of 80-100 mL/min. Tenax®-GC is thermally conditioned at 220°C for 8-12 hours at a nitrogen flow rate of 80-100 mL/min. The actual length of time required for the conditioning period may be determined based on the adequacy of the resulting blank checks of the conditioned tubes. Method 5041 (modified to use a sorbent desorption temperature of 250°C) and Method 8260 may be used to perform a blank check of each set of sampling tubes to ensure cleanliness.

7.1.2 An acceptable blank level is less than or equal to ($\leq$) Method Detection Limits for Method 5041/8260 (see Method 8260 for Method Detection Limits). A general guideline of analyte values less than 2 ng for any volatile organic compound may be used as a criterion of cleanliness.

7.1.3 After conditioning, tubes are sealed and placed on cold packs or ice (maintained at a temperature less than 10°C) until sampling is completed. Conditioned tubes should be held for no more than 14 days before sampling, to prevent the possibility of contamination.

7.2 Pretest preparation

7.2.1 All train components should be cleaned and assembled as previously described. A dry gas meter should be calibrated within 30 days prior to use, using a standard orifice, or other approved calibration device/meter.

7.2.2 The SMVOC is assembled according to the schematic diagram in Figure 1. Cooling water should be circulated to the condensers and the temperature of the cooling water must be low enough to maintain the temperature of the gas entering the sorbent below 20°C.

7.3 Leak-checking

7.3.1 To leak-check the entire train, it is necessary to leak-check from the probe to the pump. In order to adequately represent actual sampling conditions, a leak-check should be performed with the pump on and the leak rate measured in liters per minute (Lpm) on the dry gas meter. After the desired vacuum is reached, the pump is isolated from the train to check for leaks.

7.3.2 Ensure that all connections are tight and that the train is assembled correctly with sorbent cartridges properly assembled and in the right direction for sampling. Seal the end of the probe and turn the isolation valve to the sample open position. Turn on the pump and adjust the vacuum to 25.4 cm above normal operating pressure (38 cm Hg should be sufficient as 12.7 cm or less is normal). Prior to leak-checking, verify that both the coarse and fine adjust valves on the meter box are partially opened to prevent backflushing of any condensate during final leak checks as the fine adjust valve will need to be adjusted to increase vacuum rather than decrease vacuum. Allow the rotameter on the meter box to drop to zero, allow the dry gas meter to stop, and the pressure on the water column gauge (represents the pressure inside the dry gas meter) to stabilize. The pump is isolated from the train by shutting off the coarse adjust valve. Record the leak rate directly from the vacuum gauge and time for one minute. The leak rate must be less than 0.02 Lpm for 1 Lpm sampling and 0.01 Lpm for sampling at a lower rate.

7.3.3 Upon completion of the leak check, turn off the pump and release the pressure/vacuum in the train by turning the isolation valve to the vacuum release position and allowing ambient air (filtered with charcoal or equivalent) to enter the train. The initial leak check should be above normal operating pressure. The final leak check (following collection of 20 L of sample) should be at least at the highest vacuum encountered during the run.

NOTE: The volume of air pulled through the SMVOC during leak-checking procedures prior to sampling should be less than 2.5% of the total volume sampled. If a volume greater than 2.5% of the total sampling volume is pulled through the SMVOC in obtaining a successful leak check, the sorbent tubes used during this leak check must be discarded and a successful leak check with a minimum volume of gas pulled through the train must be obtained with a new set of sampling tubes in place.

7.4 Sample collection - Sample collection procedures are described in Sec. 6.5.

7.5 Analytical procedure - Samples are analyzed by Methods 5041 and 8260. In these methods, adapted for a three-tube SMVOC, the Tenax® sorbent tubes are spiked with surrogates, internal standards are spiked into the purge water, and the tube(s) thermally desorbed at 250°C under a purge of organic-free helium. The tubes may all be analyzed individually, or the Tenax® tubes may be analyzed as a pair with the Anasorb® tube analyzed separately, or multiple tubes may be combined on one trap for analysis in order to decrease detection limits. The gaseous effluent from the tubes is bubbled through purged organic-free reagent water (Sec. 5.6) and trapped on an analytical sorbent trap in a purge-and-trap unit. After desorption, the analytical sorbent trap is heated rapidly and the gas flow from the analytical trap is directed to the head of a wide-bore capillary column (Method 5041) under subambient conditions. The volatile organic compounds desorbed

from the analytical trap are separated by temperature-programmed gas chromatography and detected by continuously-scanning low resolution mass spectrometry (Method 8260). Concentrations of volatile organic compounds are calculated from a multipoint calibration curve, using the method of response factors. Refer to Method 8260 for details.

7.6 Calculations

7.6.1 The following nomenclature is used in the calculation of sample volume:

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm (in.) Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

T_m = Dry gas meter average absolute temperature, °K (°R)

T_{std} = Standard absolute temperature, 293°K (528°R)

V_m = Dry gas volume measured by dry gas meter, dcm (dcf)

γ = Dry gas meter calibration factor

$V_{m_{(std)}}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf)

7.6.2 The volume of gas sampled is calculated as follows:

$$V_{m_{std}} = V_m \gamma \frac{T_{std} P_{bar}}{T_m P_{std}} = K_1 \gamma \frac{V_m P_{bar}}{T_m}$$

where:

K_1 = 0.3858°K/mm Hg for metric units or

K_1 = 17.64°R/in. Hg for English units.

7.6.3 The concentration of volatile organic compound (CPD) in the stack sample (C_g) is calculated as follows:

$$C_g = \frac{\text{Total weight of CPD in sample, µg (i.e., VOST tubes + condensate)}}{\text{Volume of sample at standard conditions, dscm}}$$

If all three sorbent tubes and the condensate are analyzed separately, four sample results (fewer if some tubes are analyzed together) must be added together to obtain the total weight of CPD. If a measurable amount of the compound is found in one or more fractions of the sample, but the amount in one or more of the other fractions is below detection limit, the following strategy is recommended, but is subject to being overruled by regulatory authorities. Count the "sum of the nondetects" as zero if the sum of the detection limits (in nondetect fractions) is less than 10% of the total of the detected amount from the other fractions. In

cases where the sum of the detection limits in the nondetect fractions is greater than 10% of the amount quantitated in the other fractions, then report the total CPD as greater than the detected amount but less than the detected amount plus the sum of nondetect fraction detection limits.

8.0 QUALITY CONTROL

8.1 Prior to actual sampling on-site, all of the applicable sampling equipment should be thoroughly checked to ensure that each component is clean and operable. Each of the equipment calibration data forms should be reviewed for completeness and adequacy to ensure the acceptability of the equipment. Each component of the sampling system should be carefully packed for shipment. Upon arrival on-site, the equipment should be unloaded, inspected for possible damage, and then assembled for use.

8.2 The following quality control (QC) checks are applicable to the sampling procedures:

8.2.1 Each sampling train must be visually inspected for proper assembly before every use.

8.2.2 All sampling data should be recorded on standard data forms which may serve as a pretest checklist.

8.2.3 The temperature measurement system should be visually checked for damage and operability by measuring the ambient temperature.

8.2.4 All sampling data and calculations should be recorded on preformatted data sheets.

8.2.5 All glassware for SMVOC should be cleaned according to the procedure in Sec. 6.1.

8.2.6 Ten percent of the SMVOC tubes should be subjected to GC/MS QC measurements. No analytes should be detected at concentrations above method detection limits in unused SMVOC tubes. If these quality control tests are performed by the manufacturer, documentation should be obtained from the commercial supplier and retained.

8.2.7 All cleaned glassware, hardware, and prepared sorbent traps should be kept closed with ground-glass caps or Teflon® tape until assembly of the sampling train in the field. The sorbent traps should be recapped immediately after each set of samples is collected.

8.2.8 Prior to sampling, the Tenax®-GC and Anasorb®-747 tubes should be spiked with the compounds of interest to ensure that they can be thermally desorbed under laboratory conditions. This spiking is necessary but not sufficient. The compound must still be sampled from the source.

8.2.9 Assembly and recovery of the sampling trains must be performed in an environment as free from uncontrolled dust and solvent vapors as possible.

8.2.10 Blanks (field, trip, laboratory) must be collected.

8.2.11 The entire sampling train should be leak-checked before and after each run. If the sampling train is moved from one sampling port to another during a run, the train should be leak-checked before and after the move.

8.2.12 Dry gas meter readings, temperature readings, and pump vacuum readings should be made during sampling and recorded in intervals no greater than 5 minutes.

8.2.13 Sorbent traps should be used for sampling within two weeks of preparation.

8.2.14 During sample collection, the gas stream temperature at the inlet to the first sorbent trap must be maintained at or below 20°C.

8.2.15 All sample traps should be stored under refrigeration or on ice or cold packs (temperature maintained less than 10°C) until ready for analysis.

8.3 QC for analytical procedures

8.3.1 Calibration standards should be prepared at five different concentration levels for each analyte of interest. Compounds of interest, surrogate compounds, and internal standards are spiked into the purge water for generation of a multipoint calibration curve. When samples are analyzed, surrogate compounds are spiked onto the sampling tubes using flash vaporization techniques (Method 5041), but internal standards are spiked into the purge water. Response factors for each compound are calculated and these response factors are used for the calculation of analytical results. Refer to Methods 5041 and 8260 for detailed analytical QC procedures for analysis of samples.

8.3.2 To establish the precision and accuracy of the analysis, triplicate paired Tenax®-GC tubes should be spiked with analytical surrogate volatile organic compounds using flash evaporation and analyzed immediately following the initial calibration and before sample analysis. The spiking level should be at the expected level of volatile organic compounds in the stationary source. The spiking standard must be prepared from stock standards separate from those used for calibration. Recovery for each volatile organic compound and surrogate should be within 50% to 150% of spiked value. The relative standard deviation associated with each analyte should be less than 25 percent.

8.3.3 The average recovery from the initial precision and accuracy determinations should be used as an acceptance criterion for sample results. The surrogate recovery in each sample should be within three standard deviations of the average recovery obtained from the initial precision and accuracy determinations.

8.3.4 An EPA performance audit should be completed during a trial burn as a check on the entire SMVOC system. The audit results should agree within 50% to 150% of the expected value for each specific compound of interest. This audit consists of collecting a gas sample containing one or more volatile organic compounds in the SMVOC from an EPA audit gas cylinder. Collection of the audit sample in the SMVOC may be conducted either in the laboratory or at the field test site. Analysis of the SMVOC audit sample must be by the same person, at the same time, and with the same analytical procedure as used for the regular SMVOC samples from the field test.

9.0 METHOD PERFORMANCE

See Method 8260.

10.0 REFERENCES

1. McGaughey, J.F., Bursey, J.T., Merrill, R. G., "Field Test of a Generic Method for Halogenated Hydrocarbons: A VOST Test at a Chemical Manufacturing Facility Using a Modified VOST Sampling Method", EPA-600/R-94/130, PB95-142055, U.S. EPA, Research Triangle Park, NC, July 1994,

2. Johnson, L.D., Fuerst, R.G., Foster, A.L. and Bursey, J.T.,"Replacement of Charcoal Sorbent in the Sampling of Volatile Organics from Stationary Sources," Intern. J. Environ. Anal. Chem.,Vol 62, pp. 231-244 (1996).

3. Foster, A.L. and Bursey, J.T., VOST Charcoal Specification Study, EPA-600/R-96/051, PB96-175252, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1996.

TABLE 1

HIGH VOLATILITY ORGANIC COMPOUNDS[a]

Compound	Boiling Point
Bromomethane	4°C
Chloroethane	12°C
Vinyl bromide	16°C, at 750 mm
Vinyl chloride	-13.4°C

[a]Use of SLO-SMVOC may be helpful.

TABLE 2

COMPOUNDS FOR WHICH METHOD 0031 IS NOT APPLICABLE

Compounds	Boiling Point	Comment
Allyl chloride	45°C	Reactive compounds; interacts with test matrix to yield poor recoveries and poor reproducibility
Acetone	56°C	Polar, water soluble
Methyl ethyl ketone	80°C	Polar, water soluble
Chloromethane	-24°C	Reactive compounds; interacts with test matrix to yield poor recoveries and poor reproducibility
Epichlorohydrin	116°C	Not amenable to SMVOC analytical procedure
Chloromethyl methyl ether	56°C	Not amenable to SMVOC analytical procedure
Bis(chloromethyl) ether	106°C	Not amenable to SMVOC analytical procedure
Acetonitrile	82°C	Polar, water soluble
Acetaldehyde	21°C	Polar, water soluble, reactive
Acrolein	53°C	Polar, water soluble, reactive
Methanol	65°C	Polar, water soluble
Ethanol	78°C	Polar, water soluble
Isopropyl alcohol	82°C	Polar, water soluble

FIGURE 1
SCHEMATIC OF SAMPLING METHOD FOR VOLATILE
ORGANIC COMPOUNDS (SMVOC) TRAIN

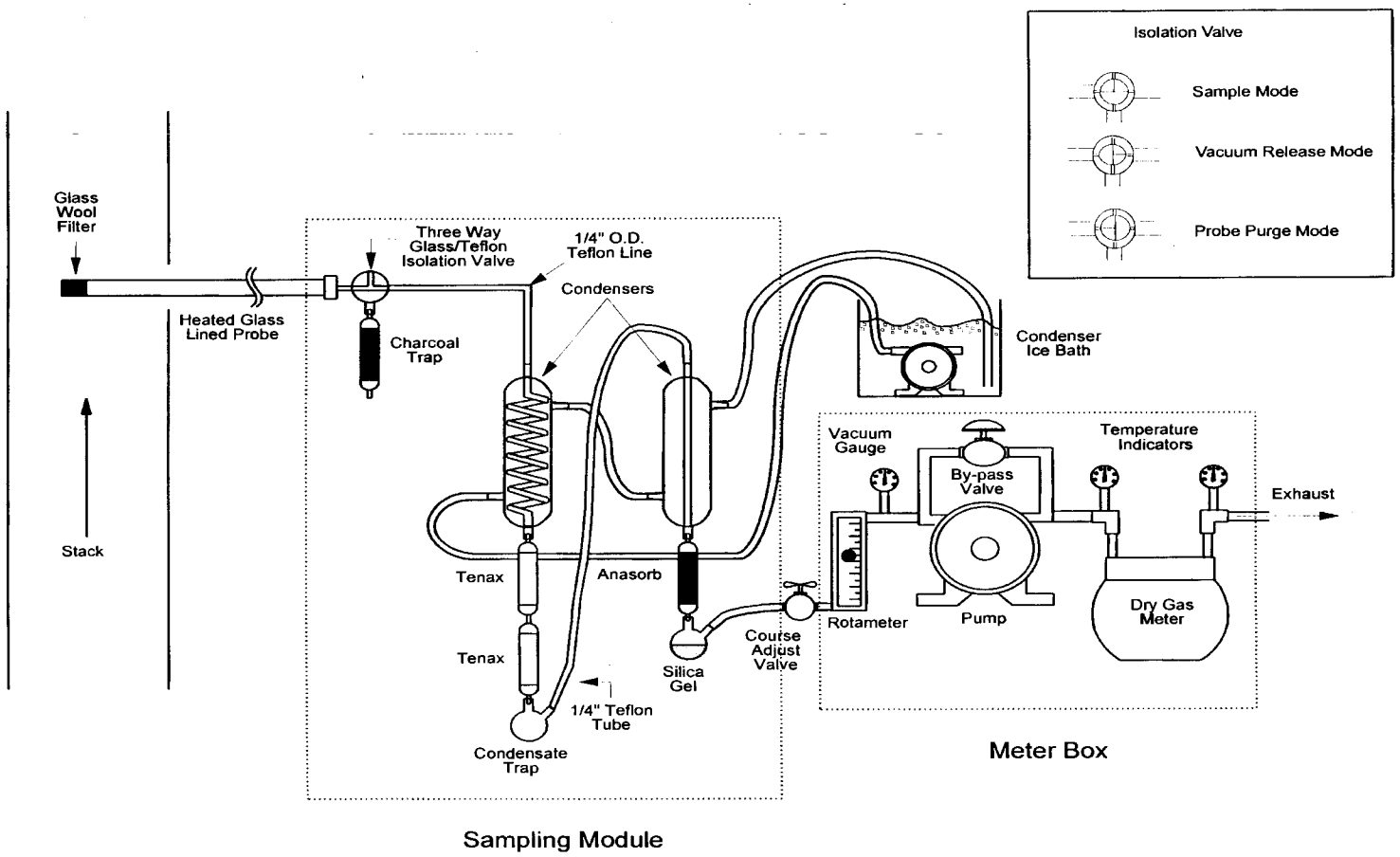
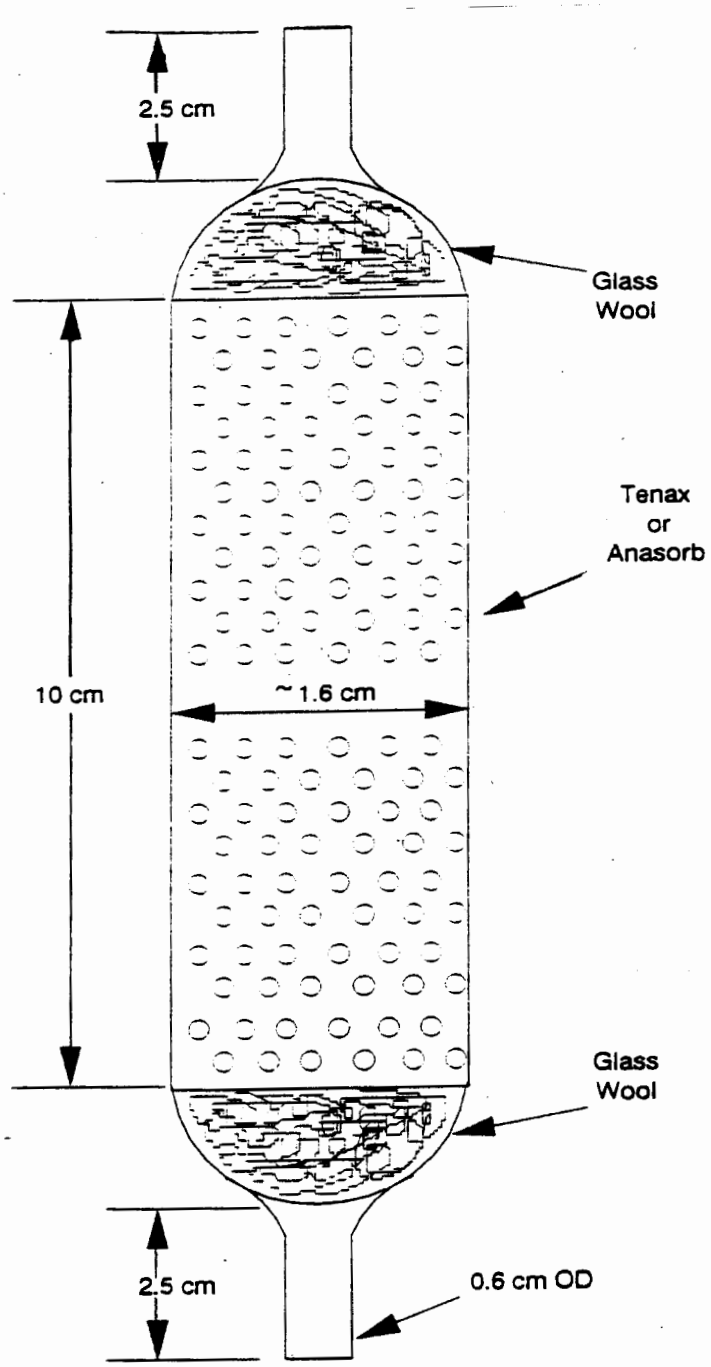


FIGURE 2
SMVOC TUBE



SAMPLING OF PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS FROM COMBUSTION SOURCES USING TEDLAR® BAGS

1.0 SCOPE AND APPLICATION

1.1 This method establishes standardized test conditions and sample handling procedures for the collection of volatile organic compounds collected from effluent gas samples from stationary sources, such as hazardous waste incinerators and other combustion sources, using time-integrated evacuated Tedlar® bags. As indicated, the first group of compounds listed below have met Method 301 (Ref. 6) acceptance criteria in a field method evaluation study. The second group of compounds did not meet Method 301 criteria, and the third group of compounds have been identified as candidate analytes from the literature but have not been tested. This is a sample collection method and does not directly address the analysis of these samples. Gas chromatography/mass spectrometry (GC/MS) (Method 8260) is the recommended analytical technique because of its ability to provide positive identification of compounds in complex mixtures such as stack gas.

Compound	CAS Registry No.
Compounds that Met Method 301 Acceptance Criteria in a Field Method Evaluation	
1,1,1-Trichloroethane	71-55-6
Trichloroethene	79-01-6
1,1-Dichloroethane	75-34-3
1,1-Dichloroethene	75-35-4
2,2,4-Trimethylpentane	540-84-1
Allyl chloride	107-05-1
Benzene	71-43-2
Carbon tetrachloride	56-23-5
Methyl chloride	74-87-3
n-Hexane	110-54-3
Methylene chloride	75-09-2
Toluene	108-88-3
Trichlorofluoromethane	353-54-8
Vinyl bromide	593-60-2
Vinyl chloride	75-01-4
Compounds that Did Not Meet Method 301 Acceptance Criteria in a Field Method Evaluation	
Methyl bromide	74-83-9
1,3-Butadiene	106-99-0
Dichlorodifluoromethane	75-71-8
Appropriate Candidate Compounds Not Tested in the Field	
1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2
1,1,2-Trichlorotrifluoroethane	76-13-1
Chloroform	67-66-3
1,2-Dichloropropane	78-87-5
Tetrachloroethene	127-18-4

1.2 This method is not applicable to the collection of samples in areas where there is an explosion hazard. Substitution of intrinsically safe equipment or procedures for the equipment or procedures described in this method will not be sufficient to adapt this method for use in areas where there is an explosion hazard. Additional modifications to the sampling and analytical protocols may be required.

1.3 This method does not employ isokinetic sampling and therefore is not applicable to the collection of highly water soluble volatile organic compounds contained in an aerosol of water. This method uses either a constant or proportional rate sampling, depending upon the extent of the variability of the emission flow rate.

1.4 This method is restricted to use by, or under the close supervision of, trained analytical personnel experienced in sampling organic compounds in air. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 Each compound for which this method can be considered shall meet the criteria listed in Secs. 1.5.1 - 1.5.3, below. Table 1 provides boiling points, condensation points (calculated from vapor pressure) at 20°C (72°F), and estimated instrument detection limits for compounds for which applicability of the method has been demonstrated. This method is not limited to the compounds in the target analyte list, however, stability and recovery shall be demonstrated when compounds other than those listed in Sec. 1.1 are to be sampled.

1.5.1 The compound must have a boiling point < 121°C.

1.5.2 The compound must have a concentration in the stack gas below the condensation point.

1.5.3 During validation studies, the loss of the compound from a Tedlar® bag must be less than 20% over a 72-hour storage time at temperatures above 0°C.

1.5.4 This method is not applicable to sources that are under vacuum. Under conditions of sufficiently high positive pressure, it may be possible to force sample gas into the Tedlar® bag causing the gas volume in the bag to be biased high versus the actual meter reading.

2.0 SUMMARY OF METHOD

2.1 A representative sample is drawn from a source through a heated sample probe and filter.

2.2 The sample then passes through a heated 3-way valve and into a condenser where the moisture and condensable components are removed from the gas stream and collected in a trap.

2.3 The sample is collected in a Tedlar® bag held in a rigid, air-tight opaque container.

2.4 The dry gas sample and the corresponding condensate are then transported together to a GC/MS. A mass spectrometer is most suited for the analysis and quantitation of complex mixtures of volatile organic compounds. The total amount of the analyte in the sample is determined by summing the individual amounts in the bag and condensate. A flow chart of the procedure is given at the end of this method.

3.0 INTERFERENCES

3.1 The materials from which the Tedlar® bag is constructed may contribute background hydrocarbon contamination. Purging the bag with air or N_2 may reduce the concentration of these hydrocarbons. Exposure of the bag to direct sunlight may increase the concentration of these hydrocarbons. Therefore, the bag must be protected from exposure to sunlight by using an opaque container to house the bag during sampling and shipping.

3.2 Components of the source emissions other than the target compounds may interfere. Interferents may be differentiated from the target compounds during mass spectrometric analysis.

3.3 Common problems that can invalidate Tedlar® bag sampling data and techniques to remedy these problems are listed in Table 2.

3.4 Available stability data suggest that this method may not perform well in sampling streams containing polar and reactive compounds like methyl ethyl ketone, formaldehyde, methanol, 1-butene, and acetone. The use of this method to sample these compounds needs to be evaluated before sampling.

4.0 APPARATUS AND MATERIALS

4.1 Tedlar® bag sampling train - A detailed schematic of the principal components of the sampling train is shown in Figure 1.

4.1.1 The sampling train (Figure 1) consists of a glass-lined probe, a heated glass or Teflon® filter holder and quartz filter attached to one of two inlets of a glass and Teflon® 3-way isolation valve (Figures 2 and 3). The purge line is connected to a charcoal trap and a silica gel trap, which filters incoming air. The outlet of the isolation valve is connected to a glass, water-cooled coil-type condenser and a glass condensate trap for removal and collection of condensable liquids present in the gas stream. A 1/4-in. OD x 1/8-in. ID Teflon® transfer line connects the condensate trap to a second 3-way isolation valve and the isolation valve to a Tedlar® bag contained in a rigid, air-tight container for sampling, storage, and shipping. The bag container is connected to a control console with 1/4-in. OD x 1/8-in. ID vacuum line by means of 1/4-in. Teflon® connectors at each end. A silica gel trap is placed in the vacuum line between the bag container and the control console to protect the console from moisture during sampling.

4.1.2 The vacuum required to operate this system is provided by a leak-free diaphragm pump contained in the control console (Figure 4). When the pump is turned on, the space between the inner walls of the bag container and the Tedlar® bag is evacuated, placing the system under negative pressure, which pulls the sample through the sampling train and into the Tedlar® bag. The sampling train vacuum is monitored with a vacuum gauge installed in-line between the vacuum line and the coarse adjustment valve mounted in the control console.

4.1.3 Sample flow rate is regulated by adjusting the coarse and fine valves on the control console. The coarse adjustment valve controls the sample inlet volume and rate and isolates the vacuum line, vacuum gauge, and sample train from the pump and other console components during leak checks. Sample volume is monitored by a rotameter, contained in the control console and installed on the outlet side of the dry gas meter.

4.1.4 The source, probe, filter, and condenser temperatures are monitored by Type J or K thermocouples using the temperature readout in the control console. Probe heater temperature is regulated by the temperature controller provided in the control console.

4.1.5 The velocity pressure and temperature of the source gases are measured using a standard or S-type pitot tube connected to a manometer with 1/4-in. OD x 1/8-in. ID tubing, in accordance with Method 2 (see Ref. 9). The source velocity pressure and temperature must be monitored during sampling and the sampling rate adjusted proportionally to changes in the flue gas velocity (Sec. 7.5.2.1).

4.2 Sample train components

4.2.1 Probe assembly - The probe assembly consists of a length of heated and insulated borosilicate glass tube inside a length of stainless steel tubing. The probe temperature shall be maintained between 130°C and 140°C (266°F and 284°F) in order to prevent damage to Teflon® lines and to facilitate efficient cooling of the gases in the condenser. The stainless steel sheath must be cooled with water when the source temperature approaches or exceeds 140°C (284°F).

4.2.2 Particulate filter - Particulate matter from the sample gas stream exiting the probe is collected on a quartz filter substrate in a heated 47-mm Teflon® or glass filter holder. Use clean filters in order to prevent sample contamination. The particulate matter itself is not analyzed or archived. However, removal of the particulate matter provides a cleaner sample for analysis. All connections between the probe and particulate filter shall be heated to maintain the temperature between 130°C and 140°C (266°F and 284°F) so that the compounds remain in the volatile phase. Heat-wrapped Teflon® unions with stainless steel nuts and Teflon® ferrules are recommended for all heated connections.

4.2.3 Isolation valves - A typical isolation valve is shown in Figure 2. The isolation valves shall be constructed of Teflon® or glass with Teflon® stopcocks to provide gas-tight seals without the use of sealing greases. The probe and bag isolation valves are of identical design and materials and are therefore interchangeable. The probe isolation valve provides for the attachment of a charcoal or similar purge trap to allow filtered ambient air to enter the train when returning the train to ambient pressure after leak checks. This valve directly connects the probe and filter assembly to the condenser inlet and must be heated to between 130°C and 140°C (266°F and 284°F). The bag isolation valve allows the bag to be opened for sampling or evacuation and isolated and sealed for leak checks or system purges.

4.2.4 Condenser - Use a jacketed, water-cooled, coil-type glass condenser with a jacket volume of at least 125 mL. The condenser shall have sufficient capacity to maintain the temperature of the sample gas stream between 20°C and 4°C (68°F and 39.2°F) to ensure proper removal and collection of condensable moisture in the effluent gas stream. The cooled sample gas stream temperature should not exceed the coldest temperature to be encountered during sampling, transport and storage prior to analysis. All condenser connections must form a leak-free, vacuum-tight seal without using sealing greases. Stainless steel fittings are not permitted, and Teflon® unions or washers with screw caps are recommended.

4.2.5 Condensate trap - A glass Erlenmeyer distilling flask with threaded screw cap connections, Teflon® seals, and a minimum volume of 125 mL may be used to collect condensate. All connections on the condenser and trap shall be sized to accept 1/4-in. OD x 1/8-in. ID Teflon® or glass fittings. The stem from the condenser must be positioned to within 0.5-in from the bottom of the condensate trap.

4.2.6 Sample transfer lines and connection fittings - All sample transfer lines connecting components shall be less than 5 ft long and constructed of 1/4-in. OD x 1/8-in. ID Teflon® tubing or glass. All sample lines upstream of the condenser and condensate trap must be heated and the temperature maintained between 130°C and 140°C (266°F and 284°F). Use Teflon® fittings for connections between various train components to provide leak-free, vacuum-tight connections without the use of sealing greases. New tubing, which has been cleaned according to Sec. 6.1.2, should be used for each separate test series to prevent cross contamination. Care should be used in the application of excessive heat to Teflon® fittings in order to avoid damage and subsequent failure.

4.2.7 Tedlar® storage bag - Choose a bag size according to the guidelines provided in Sec. 7.2.4. In order to minimize wall effects, the sample volume must fill at least 80% of the bag capacity. The recommended size range for bags is 25 L to 35 L. Small bags (< 25 L) are easier to store and transport but may have insufficient volume for proportional sampling. In addition, accurate volumetric measurement is difficult with smaller bags. Large bags (> 50 L) lack portability, but may be required under certain conditions, such as during proportional sampling and for sampling sources requiring high sample rates.

4.2.8 Evacuated container (bag container) - Use any rigid, air-tight metal or plastic (e.g., PVC®/Polyethylene®/Nalgene®) drums to house the Tedlar® bag during sampling, storage, and transport. The container must be constructed so that it can easily be assembled and disassembled (for bag removal). The container must be able to hold a negative pressure of at least 10 in. H_2O. The bag container must be at least 20% smaller than the Tedlar® bag being used but must be large enough to hold the volume of sample required (e.g., for a sample size of 20 L, a 25-L Tedlar® bag inside a 20-L container provides sufficient volume without danger of overinflating the bag).

Containers must not have staples, sharp edges, or metal closures which might damage bags. The container should also be constructed of a material that shields the sample from exposure to sunlight to protect the bag and its contents from ultra-violet light. A viewing port or other means of observing the flexible bag during sampling is desirable. During storage and transport, the viewing port shall be covered with opaque material.

4.2.9 Vacuum lines - Use Tygon®, Poly®, Nylon®, or similar tubing capable of maintaining at least 10-in. H_2O negative pressure without collapse as vacuum lines. Tubing should be 1/4-in. OD x 1/8 in. ID size to minimize volume and ensure compatibility of connection fittings throughout the train. Stainless steel fittings and valves may be used for vacuum line connections but may not be used in the sampling line.

4.2.10 Control console (meter system) - The metering system required for this method is readily available in the form of the control console/meter box from a Volatile Organic Sampling Train (VOST, Method 0030), and shall consist of the components pictured in Figure 4.

4.2.10.1 Vacuum gauge (meter pressure) - Use a direct reading, mechanical vacuum gauge capable of measuring a vacuum of at least 15 in. Hg with 1-in. or smaller increments to monitor the system vacuum during sampling and leak checking the bag, the container, and the sampling train.

4.2.10.2 Sample flow rate adjustment valves - Coarse and fine adjustment valves are provided. The coarse adjustment valve controls volume and rate of sample flow and isolates the control console from the sampling train and vacuum line during leak

checks. The fine adjustment valve controls sample rate and system vacuum. Closing the valve increases train vacuum and sample flow rate. Opening the valve decreases train vacuum and sample flow rate.

4.2.10.3 Pump - Use a leak-free diaphragm pump or equivalent that is capable of pulling and maintaining a vacuum of at least 15 in. Hg and a flow rate of at least 1 liter per minute (Lpm).

4.2.10.4 Calibrated dry gas meter - The control console contains a calibrated dry gas meter capable of reading 1 L per revolution with 0.1-L increments, and provides accurate measurement of the volume of the sample collected.

4.2.10.5 Flow meter - Use a rotameter with a glass tube and a glass, Teflon®, or sapphire float ball of suitable range to measure the sample flow rate. A range of ± 25% of the desired sampling rate is suggested to ensure greater accuracy of readings and a better range for adjustment of the sampling rate (proportional to the source gas stream velocity). The flow meter shall be accurate to within 5% over the selected range. The rotameter is installed at the outlet of the dry gas meter in the console.

4.2.10.6 Thermocouples and temperature read-out device - Use a sufficient number and length of Type J or K thermocouples. A multi-channel digital thermocouple read-out should be provided in the control console to display the source, probe, filter, condenser, and dry gas meter temperatures.

4.2.10.7 Heat controller - Use a rheostat or digital temperature controller (e.g., Fuji PYZ4 or equivalent) to regulate probe heat temperatures.

4.2.11 Pitot tube probe - A standard or S-type pitot tube must be used for pretest and post-test velocity traverses and to monitor flow so that the sampling rate can be regulated proportionally to the source gas velocity throughout the length of the sampling run.

4.2.12 Pressure gauge (manometer) - Use a water- or oil-filled U-tube or inclined manometer capable of measuring to at least 10 in. H_2O and accurate to within 0.1 in. H_2O for monitoring and measuring the source gas velocity.

4.2.13 Barometer - Use an aneroid or other barometer capable of measuring atmospheric pressure to within 0.1 in. Hg of actual barometric pressure.

4.2.14 Charcoal and silica gel absorbent traps - Use charcoal traps to absorb organic compounds in the atmosphere at the site and an indicating silica gel trap to absorb water. One charcoal trap is attached to the probe isolation valve and filters incoming air when releasing vacuum to prevent contamination of the train during leak checks. Any readily available, ready-made charcoal tube similar to a VOST tube may be used. The silica gel trap is used in the vacuum line to protect the pump from water.

4.2.15 Stopwatch - Use any stopwatch capable of measuring 1 second, to time sample collection.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Water - Water used for sample train preparation shall be distilled and deionized. Water used for rinses during recovery of condensate shall be prepurged high performance liquid chromatography (HPLC)-grade. Clean, clear tap water may be used as condenser cooling water.

5.3 Nitric acid, HNO_3 (10%) - reagent grade.

5.4 Charcoal - SKC petroleum-based charcoal, or equivalent. A mesh size of 6-14 is recommended. New or reused charcoal may be used for each run series or test condition. Reused charcoal must be reconditioned using the same criteria specified in VOST (Method 0030).

5.5 Silica gel - Silica gel shall be indicating type, 6-16 mesh. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

5.6 Methanol - Spectrometric-grade, or equivalent.

5.7 Field spiking standards - Appropriate gas cylinders containing the target components of interest in known concentrations (highest purity available) for field spiking.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Pretest preparation

6.1.1 Glassware - Before sampling, prepare the glass components of the train by cleaning with non-ionic detergent (e.g., Alconox) and hot water in an ultrasonic bath. Rinse each component three times with distilled, deionized water, then rinse three times with 10% HNO_3, followed by an additional three rinses with distilled, deionized water. Dry in an oven at 130°C (266°F) for 2 hours.

6.1.2 Sample lines and rigid containers - Treat all Teflon® lines, fittings, and the sample bag containers as outlined in Sec. 6.1.1, but air dry these components in an area free of organic compounds rather than in an oven. Use clean Teflon® tubing for each test series or condition. Hand wash the rigid containers.

6.1.3 Bag cleaning procedure - Ensure that all bags are clean before using them for sampling. First, flush each bag three times with high-purity nitrogen (N_2; 99.998%). Then fill each bag with N_2 and analyze the bag contents at the highest sensitivity setting using the same analytical technique that will be used for analyzing samples. Before constructing the calibration curve, analyze one analytical system blank each day by taking the gas chromatograph through its analytical program with no sample injection. Analyze an analytical system blank again if carryover between samples is indicated. Other, less stringent, methods of cleaning and analysis may be used at the risk of overlooking important contaminants. An acceptable level of contamination will be a response less than five times the instrument detection limit or half

of the level of concern, whichever is less. Repeat the nitrogen flush as necessary until the acceptable level has been reached. No bag shall be used until it has been satisfactorily cleaned.

6.2 Sample bag storage and transport procedures - To ensure sampling integrity, perform sample recovery in a manner that prevents contamination of the bag sample. Protect the bag from sharp objects, direct sunlight and low ambient temperatures (below 0°C [32°F]) that could cause condensation of any of the analytes. Store the bags in an area that has restricted access to prevent damage to or tampering with the sample before analysis. Analyze the bag samples within 72 hours of sample collection unless it can be shown that significant (> 20%) sample degradation does not occur over a longer period of sample storage. Upon completion of the testing and sample recovery, check all the data forms for completeness and the sample bags for proper identification. Store the bags in rigid, opaque containers during all sampling, storage and transport procedures. Ship the bags using ground transportation. Follow all hazardous materials shipping procedures.

6.3 Condensate storage and transport procedures - To ensure sample integrity, perform sample recovery in a manner that prevents the contamination of the condensate (Sec. 7.6.5). Store the condensate in 40-mL vials with no headspace. Place the vials in ice or in a refrigerated container at 4°C (± 2°C) [39.2°F (±7.2°F)] immediately following recovery and during transport for analysis. In addition, store the vials in an area that has restricted access to prevent damage to or tampering with the sample before analysis. Upon completion of the testing and sample recovery, check all the data forms for completeness and the condensate samples for proper identification. Follow all hazardous materials shipping procedures.

6.4 The time lapse between sampling and analysis shall not exceed 72 hours unless it can be justified by specific sample matrix stability data that meet the criteria of Sec. 1.5.3. Stability in a Tedlar® bag shall be demonstrated by spiking analytes into inert gas in the laboratory and into stack gas in the field. The spiking level must be at least at the level found in the samples of the emissions matrix obtained during the pre-site survey. Compound recovery in both laboratory and field studies must be ≥ 80% after 72 hours for consideration of applicability.

7.0 PROCEDURE

The overall sampling procedure involves a pretest survey of the source to establish sampling parameters, a series of pretest checks of the sampling system and the source conditions, and the actual sample collection. These steps are described in Secs. 7.1 - 7.5. Following the actual sample collection step, sampling data are recorded and a post-test leak check is performed (Sec. 7.6). As noted in Sec. 1.0, this method does not include sample analysis procedures, but general guidelines for sample analysis are given in Sec. 7.7. Sec. 7.8 provides an extensive set of calculations associated with the sample collection and analysis procedures.

7.1 Pretest survey

7.1.1 Perform a pretest survey for each source to be tested. The purpose of the survey is to obtain source information to select the appropriate sampling and analysis parameters for that source. Potential interferences may be detected and resolved during the survey. When necessary information about the source cannot be obtained, collection and analysis of actual source samples may be required.

Use the pretest survey data form (Figure 5) to record information gathered during the pretest survey.

7.1.2 The following information must be collected during a survey before a test can be conducted. The information can be collected from literature surveys and source personnel, but an actual on-site inspection is recommended. A copy of the survey results must be forwarded to the staff performing the sample analyses.

7.1.2.1 Determine whether the sampling site is in a potentially explosive atmosphere. If the sample site is located in an explosive atmosphere, use other, intrinsically safe test methods. This method is never to be used in a potentially explosive atmosphere (Sec. 1.2).

7.1.2.2 Measure and record the stack dimensions. Select the sampling site and the gaseous sampling points according to Method 1 (Reference 9) or as specified by the regulatory personnel.

7.1.2.3 Determine the stack pressure, temperature, and the range of velocity pressures using Method 2 (Reference 9). A source with a negative pressure is not suitable for this method.

7.1.2.4 Determine the stack gas moisture content (Sec. 7.2.3) using Approximation Method 4 (Reference 9) or its alternatives. Perform the determination when process operations are as they will be during final sampling. If the process uses and emits ambient air, use a sling psychrometer to measure the moisture content of the ambient air in the area of process air uptake.

7.1.2.5 In accordance with Method 1, select a suitable probe liner and probe length as determined by the temperature and dimensions of the source. Determine the point within the stack that represents an average flow and temperature of the stack. Mark the probe at the determined distance to provide a reference point. For sample collection, insert the probe into the duct to the predetermined point to ensure proper probe placement and collection of a representative sample.

7.1.2.6 Determine whether the source has a constant or variable gas flow rate. The flow rate may be considered constant if the variation over the sampling period is no more than 20%. If the process is constant, use a constant sampling rate (Sec. 7.5.1). If the process is not constant, use proportional sampling (Sec. 7.5.2).

7.1.2.7 Determine approximate levels of target compounds by collecting a pretest bag sample for analysis. This information is needed to establish parameters for the analytical system.

7.1.2.8 Check the sampling site to ensure that adequate electrical service is available.

7.1.2.9 Follow all guidelines in the health and safety plan for the test. Use appropriate safety equipment as required by conditions at the sampling site (e.g., respirator, ear and eye protection, and a safety belt).

7.2 Pretest procedures

7.2.1 Assemble the train according to the diagram in Figure 1. Adjust the probe, filter, and valve heater controls to maintain a temperature between 130°C and 140°C (266°F and 284°F). Circulate cooling water from an ice bath to the condenser until the temperature is

stabilized at or below 20°C (68°F). Allow the probe, filter, valve, and condenser temperatures to stabilize before sampling. Mark the probe, pitot tube, and thermocouple assembly with the proper sampling points as determined in accordance with Method 1. Before sampling, insert the pitot tube and thermocouple probe into the stack, to allow the thermocouple readings to stabilize.

7.2.2 Preliminary velocity and temperature traverse - While the probe, filter, valve, and condenser temperatures are stabilizing, perform a preliminary velocity/temperature traverse in accordance with Methods 1 and 2. Record the velocity (ΔP) and temperature (T, °C) at each point to determine a point of average flow and velocity and measure the static pressure at that point. Determine the average velocity head (ΔP_{avg}) and range of fluctuation.

7.2.3 Determination of moisture content - Determine the moisture content of the gas stream being sampled before (Sec. 7.1.2.4) or during actual sampling. For combustion of water controlled processes (wet electrostatic precipitators and scrubbers), obtain moisture content of the flue gas during test conditions from plant personnel or by direct measurement using Method 4.

7.2.4 Criteria for selection of sample volume and flow rate - The flow rate should fill the bag to at least 80% of its capacity during the sampling period. The following criteria should be met:

7.2.4.1 Minimum stack sampling time for each run should be 1 hr. Data from less than 1 hr of sample collection would be an invalid test run. Two hours of stack sampling time is recommended as optimal.

7.2.4.2 The minimum sample volume shall be at least 15 L.

7.2.4.3 The minimum sample flow rate shall be 250 mL/min.

7.2.4.4 Typically, the average sampling flow rate is about 0.5 L/min, which will collect approximately 30 L of sample per hour.

7.2.4.5 Mass emission rate determination - Determine whether the final result will be presented on a concentration or mass emission basis before sampling. If results will be presented on a concentration basis, only the concentrations of the target analytes and the stack gas moisture content need to be measured. If the mass emission rate of any compound is to be presented, the volumetric flow rate of the stack gas must also be determined. The volumetric flow rate may be determined by performing a temperature and velocity traverse in accordance with Methods 1 and 2, with actual sample collection.

7.3 Leak check procedures

7.3.1 Bag evacuation and bag leak check procedure - Before sampling, ensure that the Tedlar® bag is fully evacuated and leak free.

7.3.1.1 Assemble the sampling train as illustrated in Figure 1 and described in Sec. 4.1.1, ensuring that all connections are tight.

7.3.1.2 Disconnect the vacuum line from the bag container and attach this quick connect fitting to the quick connect fitting on the outlet of the bag isolation valve (Figure

1) and turn on the pump in the control console (Figure 1). Turn bag isolation valve to position 1(Figure 3) and turn on the pump in the control console (Figure 4).

7.3.1.3 Open the coarse adjustment valve and adjust the fine adjustment valve on the control console (Figure 4) until the vacuum gauge reads 5 in. Hg.

7.3.1.4 Observe the dry gas meter and rotameter on the control console as the bag is evacuated. The bag is completely evacuated when no flow is indicated on the dry gas meter and the vacuum rises to 5 in. Hg.

7.3.1.5 Allow the rotameter float ball to drop to zero. Time and record the leak rate using the following procedure.

7.3.1.5.1 Timed leak rate - Observe the leak rate indicated on the vacuum gauge and time for 1 min. The leak rate must be less than 0.1 in. Hg.

7.3.1.6 If all connections are found to be leak tight and the leak rate cannot meet the set criteria, discard the bag and test another clean bag.

7.3.1.7 Turn the bag isolation valve to position 3 (Figure 3) to seal the evacuated bag.

7.3.1.8 Turn off the pump.

7.3.2 Pretest leak check

7.3.2.1 Before sampling and immediately after evacuating and leak checking the bag, perform a pretest leak check of the sampling train.

7.3.2.2 Ensure that the bag isolation valve is in position 3 (Figure 3) and the end of the probe is sealed.

7.3.2.3 Turn the probe isolation valve to position 2 (Figure 3), turn the pump on, and open the coarse adjustment valve(Figure 4).

7.3.2.4 Allow the sampling train to evacuate and adjust the fine adjustment valve to increase the vacuum to 5 in. Hg.

7.3.2.5 When the rotameter drops to zero and the dry gas meter slows to a stop, time and record the leak rate following the procedure outlined in Sec. 7.3.1.5.

7.3.2.6 If the leak rate is greater than 0.1 in Hg/min, check all connections, valves, and the probe seal for tightness. Any leak found must be corrected and the leak check repeated before sample collection begins. It is suggested that new fittings and connections be used when the train is assembled. During the testing, replace as necessary.

7.3.2.7 After completing a satisfactory leak check, return the sampling train to ambient pressure by turning the probe isolation valve to position 3 and turning off the pump.

7.3.2.8 When the vacuum gauge drops to zero, immediately turn the probe isolation valve to position 1. Disconnect the vacuum line from the bag isolation exit quick connect fitting, then attach the vacuum line to the bag container to return the system to the initial state described in Sec. 4.1.1 (Figures 1 and 3).

7.3.3 Post-test leak check

7.3.3.1 A post-test leak check must be performed after each bag sample is collected, before changing the bag and container for the next sample.

7.3.3.2 Ensure that the bag isolation valve is in position 1 (Figure 3) and and the probe isolation valve is in position 1 and the pump is turned off when sample collection is completed.

7.3.3.3 Remove the probe from the stack and seal the end of the probe with a leak-tight seal. Check all connections and train components for looseness or breakage. Do not tighten any connections. Record any abnormal conditions.

7.3.3.4 Disconnect the vacuum line from the container and attach to the outlet of the big isolation valve. Turn the probe isolation valve to position 2. Turn on the pump and adjust the fine adjustment valve until the train vacuum reaches at least 1 in. Hg above the highest vacuum attained during sample collection. Time and record the leak rate as previously outlined in Sec. 7.3.1.5.

7.3.3.5 If the leak rate is less than 0.1 in. Hg/min., the sample is considered valid (Secs. 7.3.1.5.1).

7.3.3.6 Return the sample train to ambient pressure (Secs. 7.3.2.7 and 7.3.2.8) and disconnect the sample and vacuum lines from the bag and container to prepare the train for the next sample.

7.3.3.7 If the post-test leak check proves invalid, discard the invalid sample. Attach a new Tedlar® bag, evacuate and leak check the bag, and repeat the sample collection.

7.4 Preparation for sample collection

7.4.1 Perform the pretest leak checks outlined in Sec. 7.3.

7.4.2 Remove the seal from the end of the probe and insert the probe into the stack to the point of average velocity and temperature and constant flow.

7.4.3 Purge the sampling train (probe, valve, and filter assembly ONLY) using the following procedures.

7.4.3.1 Disconnect the vacuum line quick connect fitting from the rigid bag container (the quick connect fitting has a valve to seal the line).

7.4.3.2 Connect the purge line from the probe isolation valve tee to the vacuum line using the quick connect fittings (Figure 1).

7.4.3.3 Ensure that the probe isolation valve is in position 1 (Figure 3), and turn on the pump.

7.4.3.4 Draw at least eight times the sample volume of flue gas, or purge for at least 10 minutes, whichever is greater.

7.4.4 Adjust the sample flow rate to the desired setting and check all temperature and flow readings during the purge to ensure proper settings.

7.4.5 Purge the sampling train before and between the collection of each sample during the test run.

7.4.6 Label each bag/container and VOA vial clearly, uniquely, and consistently with its corresponding data form and run. Follow appropriate traceability requirements as defined by the regulatory personnel. Return the train to the initial configuration described in Section 4.1.1 (Figure 1) before collecting a sample. First, disconnect the vacuum line quick connect fitting from the purge line quick connect fitting, then reconnect the vacuum line quick connect fitting to the bag container.

7.5 Sample Collection

Start sample collection after the pretest leak check (Sec. 7.3.2) and the system purge (Sec. 7.4). Collect the sample using proportional rate sampling if the pretest survey measurements (Sec. 7.1.2.7) show that the emission flow rate varies by more than 20% over the sampling period. Otherwise, use constant rate sampling. Prepare for sample collection for either method by turning the probe isolation valve to position 2 for sampling and the bag isolation valve to position 2 while the pump is still running from the system purge.

If a viewing port has been incorporated in the bag container design, visually inspect the Tedlar® bag frequently during the sampling run to ensure that it is filling properly and that a sufficient sample volume is collected. This frequent inspection will also help prevent overfilling and bursting the bag during sampling. Use the field sampling data form (Figure 6) to record sample collection data.

7.5.1 Constant rate sampling

7.5.1.1 Place the end of the probe at a point within the duct determined to have the average velocity and temperature and a constant flow rate.

7.5.1.2 Record the start volume from the dry gas meter and begin timing the sample period.

7.5.1.3 Take flue gas velocity and temperature readings using either Method 2A for smaller ducts (< 24 inches) with a remote pitot tube and thermocouple or Method 2 for larger ducts (> 24 inches). Utilizing a sample probe with pitot tubes and thermocouples attached will generally ease sampling and will provide a direct means to monitor flue gas velocity and temperature at the sample probe inlet.

7.5.1.4 Record all required data upon starting, and at intervals of no more than 5 minutes on the field sampling data form.

7.5.1.5 Adjust the sample flow rate and sampling train heating systems to the correct levels, after every velocity and temperature reading. The tester must closely monitor the sample train and control console to ensure that the sample flow rate does not vary by more than 20% during any 5-minute period.

7.5.2 Proportional sampling

7.5.2.1 Position the probe in the center of the stack.

7.5.2.2 Record the start volume from the dry gas meter and begin timing the sample period.

7.5.2.3 Monitor the velocity head during sampling as described in Sec. 4.1.5 and maintain a constant proportion between the sample flow rate and the flow rate in the duct. The flow rate to be used during sampling (Sec. 7.2.2) is calculated using the proportional sample rate equation in Sec. 7.8.4. With this equation and the sample rate assigned to the average flow rate, the rotameter setting can be determined after each velocity reading and the sample rate set accordingly.

7.5.2.4 Record all required data upon starting, and at intervals of no more than 5 minutes on the field sampling data form.

7.5.3 Single-point sampling

Collect samples from a single point within the duct as described in Secs. 7.5.1.1 and 7.5.1.2, unless multipoint sampling has been determined necessary (Sec. 7.5.4).

7.5.4 Multipoint sampling

Perform multipoint integrated sampling only in a case where there is a possibility of effluent stratification. Stratification of gases is less likely than of particulates. If however, multipoint sampling is required, determine the necessary number of sample points in accordance with Methods 1 and 2.

7.6 Post-test procedures

7.6.1 Record the final volume from the dry gas meter at the end of each sample collection period.

7.6.2 Perform a post-test leak check as described in Sec. 7.3.3.

7.6.3 Inspect the field sampling data form and sample identification labels for accuracy and completeness.

7.6.4 Replace the particulate filter after each sample.

7.6.5 Condensate Recovery - The condensate collected during sampling must be recovered separately for each individual bag sample collected, using the following procedures.

7.6.5.1 Carefully remove the condensate trap, the condenser and the sample line (from the trap to the bag) from the sample train. Pour the contents of the condensate trap into a clean measuring cylinder.

7.6.5.2 Rinse the condenser, the condensate trap and the sample line three times with 10 mL of HPLC grade water and add the rinsings to the measuring cylinder containing the condensate. Record the final volume of the condensate and rinse mixture on the field sampling data form. High moisture sources (such as those with wet control devices) may require a 150-mL or 200-mL measuring cylinder while low moisture sources (such as some rotary kilns and pyrolytic incinerators) may require only a 100-mL size.

7.6.5.3 Pour the contents of the measuring cylinder into a 20- or 40-mL amber glass VOA vial with a Teflon® septum screw cap. Fill the vial until the liquid level rises above the top of the vial and cap tightly. The vial should contain zero void volume (i.e., no air bubbles). Discard any excess condensate into a separate container for storage and transport for proper disposal.

7.6.5.4 Label each vial by using wrap-around labels. Labels can be preprinted or can be filled out on site.

7.7 Analytical Approach

The following description provides general guidelines to the analytical approach rather than a comprehensive analytical approach. The primary analytical tool recommended for the measurement of volatile organic compounds in source emissions is GC/MS using fused-silica capillary GC columns such as described in Method 8260. Prescreening of the sample by gas chromatography with either flame ionization (GC/FID) or, for electronegative compounds, electron capture detection (GC/ECD) is recommended because it may not only be cost effective, but will also yield information regarding the complexity and concentration of the sample. If the smallest feasible injection loop saturates the analytical system, dilutions of the sample can be made into Tedlar® bags using pure N_2 (99.998%) as diluent. Calculate the concentration of the volatile organic compounds in the gaseous emissions by using the equations (13-17) in Sec. 7.8.

7.7.1 Analysis of gaseous components - Introduce the gases into the gas chromatograph through the use of a sample loop. Use a cryogenic trap if sample concentration before analysis if necessary.

For most purposes, electron ionization (EI) mass spectra will be collected because a majority of the volatile organic compounds give characteristic EI spectra. Also, EI spectra are compatible with the NIST Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions can be used to elucidate molecular-weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification. For descriptions of GC conditions, MS conditions, internal standard usage, and qualitative and quantitative identification, refer to Method 8260.

7.7.2 Analysis of condensates - Refer to Method 5030 to analyze condensate samples by using the purge and trap technique or by direct aqueous injection. Use direct solvent injection if an organic phase is present distinct from the aqueous phase. Use dilution as necessary to prevent saturation of the analytical system.

7.8 Calculations

7.8.1 Carry out all calculations for determining the concentrations and emission rates of the target compounds. Round off figures after final calculations to three significant figures.

7.8.2 Nomenclature

A = Stack/source cross sectional area, m^2 (ft^2)

A_B = Amount of volatile organic compound in bag (ng)

A_c = Amount of volatile organic compound in condensate (ng)

A_{vol} = Amount of volatile organic compound in analytical sample (ng)

A_T = Total amount of volatile organic compound (ng), $A_B + A_C$

B_{ws} = Water vapor in the gas stream, proportion by volume (x100=% H_2O)

C_P = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

$C_{Emission}$ = Concentration of volatile organic compound in emissions (ng/mL)

C_{vol} = Concentration of volatile organic compound per volume sampled (ng/mL)

C_{spike} = Concentration of spiking standard in the Tedlar® bag (ng/mL or µg/L)

C_{stock} = Concentration of spike standard in the stack/audit cylinder.

$DV_{eff(std)}$ = Volumetric flow rate of exhaust gas,m^3/min, ft^3/min.

K_p = Pitot tube constant,

$$34.97\,\text{m/sec}\left[\frac{(\frac{g}{gmole})(mmHg)}{(K)(mmH_2O)}\right]^{1/2}$$

$$85.49\,\text{ft/sec}\left[\frac{(\frac{lb}{lbmole})(inHg)}{(^{O}R)(inH_2O)}\right]^{1/2}$$

L_a = Maximum acceptable leakage rate for a leak check following a component change; less than or equal to 0.1 in. Hg.

LDL_{vol} = Lower detectable amount of volatile organic compound in entire sampling train.

L_i = Individual leakage rate observed during the leak check conducted before to the "i^{th}" component change (i = 1, 2, 3...n), L/min.

L_p = Leakage rate observed during the post-test leak check,in. Hg/min.

Max $Mass_{vol}$ = Maximum allowable mass flow rate (g/hr [lb/hr]) of volatile organic compound emitted from the combustion source.

Max $Conc_{vol}$ = Maximum anticipated concentration of the volatile organic compound in the exhaust gas stream, g/m^3 ($lb\ ft^3$).

M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).

M_{fd} = Dry mole fraction of the flue gas.

M_s = Wet molecular weight of the flue gas, g/g-mole (lb/lb-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_g = Flue gas static pressure, mm H_2O (in. H_2O).

P_k = Specific gravity of mercury (13.6)

P_m = Dry gas meter pressure, inches H_2O

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_m = Average sampling rate, L/min.

Q_s = Calculated sampling rate, L/min.

Q_{sd} = Volumetric air flow rate, (m^3/min, ft^3/min).

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry gas meter temperature, K (°R).

T_s = Absolute average stack gas temperature, K (°R).

T_{std} = Standard absolute temperature, 293 K (528°R).

V_A = Analytical sample volume (mL).

V_B = Bag volume (mL).

V_i = Concentration of volatile organic compound (wt %) introduced into the combustion process.

V_i conc = Anticipated concentration of the volatile organic compound in the exhaust gas stream, g/L (lb/ft^3).

V_{lc} = Total volume of liquid collected in the condensate knockout trap.

V_m = Volume of gas sample as measured by dry gas meter, L.

$V_{m(std)}$ = Volume of gas sample measured by dry gas meter, corrected to standard conditions, L.

V_{spike} = Volume of gaseous or liquid spiking standard (mL)

V_{TBC} = Minimum dry standard volume to be collected at dry gas meter.

V_T = Train sample volume (mL)

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, L (ft^3).

V_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 4, m/sec (ft/sec).

WF = Mass flow rate of waste feed per hour, g/hr (lb/hr).

γ = Dry gas meter calibration factor, dimensionless.

ΔP = Actual velocity pressure, mm (in.) H_2O.

ΔP_{avg} = Average velocity pressure, mm (in.) H_2O.

ρw = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

θ_i = Sampling time interval of each successive component change, beginning with the interval between the start of the run and the first component change, min.

θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.

60 = Second/minute conversion.

100 = Conversion to percent.

7.8.3 Conversion factors

From	To	Multiply by
ft^3	L	0.02832

7.8.4 Proportional sample rate calculation. The flow rate to be used during sampling when the velocity head varies from the average is calculated using the following equation:

$$Q_s = Q_m \frac{\sqrt{\Delta P}}{\sqrt{\Delta P_{Avg}}} \quad (1)$$

7.8.5 Dry gas volume: Correct the sample measured by the dry gas meter to standard conditions (20°C, 760 mm Hg [68°C, 29.92 in. Hg]) by using the following equation:

$$V_{m(std)} = V_m \gamma \frac{T_{std}}{T_m} \frac{P_{bar} + P_M/13.6}{P_{std}} = K_1 V_m \gamma \frac{P_{bar} + P_M/13.6}{T_m} \quad (2)$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or

K_1 = 17.64°R/in. Hg for English units.

Equation 2 can be used as written, unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted before component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 2 must be modified as follows (with the approval of the appropriate regulatory personnel):

7.8.5.1 Case I (no component change made during sampling run)

Replace V_m in Equation 2 with the expression:

$$V_m - \left[(L_p - L_a)\right] \theta \quad (3)$$

7.8.5.2 Case II (one or more component changes made during the sampling run)

Replace V_m in Equation 2 with the expression:

$$V_m - \left(\sum_{i=1}^{n} (L_i - L_a)\theta_1 \right) - (L_P - L_a)\theta_p \quad (4)$$

and substitute only for those leakage rates (L_i or L_p) that exceed L_a.

7.8.6 Volume of water vapor

$$V_{w(std)} = V_{lc} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{1c} \quad (5)$$

where:

K_2 = 0.001333 m^3/mL for metric units, or

K_2 = 0.04707 ft^3/mL for English units.

7.8.7 Moisture content

$$B_{ws} = \frac{V_{w\ (std)}}{V_{m\ (std)} + V_{w\ (std)}} \quad (6)$$

7.8.8 Volumetric flow rate equations

7.8.8.1 Static pressure

$$P_s = P_{Bar} + \left(\frac{P_g}{P_k} \right) \quad (7)$$

7.8.8.2 Dry molecular weight

$$M_d = (\%\ CO_2 \times 0.44) + (\%\ O_2 \times 0.32) + [(\%\ CO + \%\ N_2) \times 0.28] \quad (8)$$

7.8.8.3 Dry mole fraction

$$M_{fd} = 1 - B_{ws} \quad (9)$$

7.8.8.4 Wet molecular weight

$$M_s = (M_d \times M_{fd}) + (18 \times B_{ws}) \quad (10)$$

7.8.8.5 Flue gas velocity

$$V_s = k_P\ C_P\ (\sqrt{\Delta P})_{avg} \left(\frac{T_{s(avg)}s}{M_s P_s} \right)^{½} \quad (11)$$

7.8.8.6 Volumetric flow rate

$$DV_{eff(std)} = 60\ V_s\ M_{fd}\ A \left(\frac{T_{std}}{T_{s(avg)}} \right) x \left(\frac{P_s}{P_{std}} \right) \quad (12)$$

7.8.9 Concentration of a volatile organic compound in the gaseous emissions of a combustion process.

7.8.9.1 Divide the amount of volatile organic compound determined through analysis by the volume of sample introduced into the analytical system to obtain concentration of the volatile organic compound in the bag or the condensate.

$$C_{vol} = \frac{A_{vol}}{V_A} \quad (13)$$

7.8.9.2 Multiply the concentration of the volatile organic compound (ng/mL) by the sample volume (bag or condensate) to determine the amount of the volatile organic compound in the bag or condensate.

$$A_B = C_{vol}\ x\ V_B \quad (14)$$

or

$$A_C = C_{vol}\ x\ V_{lc} \quad (15)$$

7.8.9.3 Sum the amount of volatile organic compound found in all samples associated with a single train.

$$A_T = A_B + A_C \quad (16)$$

The mass of each compound from the A fraction is added to that from the B fraction to obtain a train total before further calculation. If a measurable amount of the compound is found in one fraction, but the amount in the second fraction is below detection limit, the following strategy is recommended, but is subject to being overruled by regulatory authorities. Count the "nondetect" as zero if the detection limit is less than 10% of the total of the detected amount from the other fraction, but in cases where the detection limit in the second fraction is greater than 10% of the amount detected in the first fraction, then report the total as greater than the detected amount but less than the detected amount plus the second fraction detection limit.

7.8.9.4 Divide the total amount found by the volume of stack gas sampled to determine the concentration of the volatile organic compound in the gaseous emissions.

$$\frac{A_T}{V_T} = C_{Emission} \quad (17)$$

7.8.10 Concentration of the spiking standard in the Tedlar® bag

$$C_{spike} = \frac{V_{spike} \text{ X } C_{stock}}{V_B} \quad (18)$$

7.8.11 Recovery of the spiking standard from the Tedlar® bag sample

$$\% \text{ Recovery} = \frac{C_{vol}}{C_{spike}} \text{ X } 100 \quad (19)$$

8.0 QUALITY CONTROL

8.1 Quality assurance/quality control requirements before sampling

8.1.1 Pitot tube probe - Before sampling, assemble and calibrate the pitot tube probe (described in Sec. 4.2.11) in accordance with Method 2. Leak check above the static stack pressure. The pitot tube assembly must be leak free (0.00 in. H_2O in 1 minute).

8.1.2 Pressure gauge (manometer) - Calibrate the pressure gauge (described in Sec. 4.2.12) in accordance with Method 2. Leak check the pitot tubes, pressure gauge, and pitot tube lines simultaneously, as a unit, before the velocity traverse.

8.1.3 Thermocouple and temperature read-out device - Calibrate these devices (described in Sec. 4.2.10.6) within 30 days of sampling and in accordance with Method 2. The thermocouple and temperature read out must be accurate to ± 1°C.

8.1.4 Metering system - Calibrate the dry gas meter contained in the control console in accordance with the procedures outlined in Method 5. Calibrate the meter at a flow rate appropriate for the sampling rate used during the test.

8.1.5 Probe heater - Calibrate the probe heater before sample collection following procedures outlined in Method 5.

8.1.6 Barometer - Record the barometric pressure at the test site before each test. Alternatively, obtain the barometric pressure from a local weather service and correct it to the altitude of the test site if the reporting center is at a different altitude.

8.2 Blanks and field spikes

Field, trip and laboratory blanks, contamination checks and field spiked samples are required to monitor the performance of the sampling method and to provide the required information to take corrective action if problems are observed in the laboratory operations or in field sampling activities.

8.2.1 Field blanks - Take at least one field blank sample daily and per source. Collect high purity air or N_2 (99.998%) from a compressed gas cylinder in the same manner as source

emissions. Draw the air or nitrogen gas through the sampling system and into the bag. Field blank samples shall consist of the condensate and a bag sample. Transport and analyze this blank sample along with the stack gas samples. When the field blank values are greater than 20% of the stack values, flag the data. Report the field blank values with the stack gas results. A condensate blank is prepared by filling a vial with HPLC-grade water. The condensate blank is transported and analyzed with the stack gas condensate samples. When the field condensate blank values are greater than 20% of the stack values, flag the data.

8.2.2 Trip blanks - Take at least two Tedlar® bags labeled "trip blanks" and filled with an inert gas to the sampling site. These bags will be treated like any other samples except that they will not be opened during storage at the site. These bags will be subsequently analyzed to monitor potential contamination which may occur during storage and shipment.

8.2.3 Laboratory blanks - Leave two Tedlar® bags labeled "laboratory blanks" in the laboratory using the method of storage that is used for the field samples. If the field and trip blanks contain high concentrations of contaminants (i.e., greater than five times the detection limit of particular analyte), the laboratory blank shall be analyzed to identify the source of contamination.

8.2.4 Tedlar® bag contamination checks - The use of new bags for each test series is recommended. All bags must be cleaned and checked for contamination before being used for sampling (Sec. 6.1.3).

8.2.5 Field spike samples - Take at least one field spike per 10 field samples, or a minimum of one field spike per test. Spike the chosen bag sample with a known mixture (gaseous or liquid) of isotopically labeled analogs of all the target pollutants using either gaseous or liquid injection into the bag. Transport and analyze the spiked sample with the stack gas samples. Report the spike sample recoveries with the source test results. The compound recoveries in the spiked sample must be 80 - 120%. Use Equation 19 in Sec. 7.8.11 to calculate spiking compound recovery.

The spiking concentration should be at least twice the concentration anticipated in the emissions matrix. Use Equation 18 in Sec. 7.8.10 to calculate the spiking concentration. The syringe volume for the gaseous injection should not exceed 200 mL to minimize leakage through the septum after injection. For liquid injections, the volume injected must not exceed 1 mL to ensure complete volatilization. The final volume of the spiked gas must not exceed 1% of the total sample volume. Use the ideal gas equation to calculate the volume of gas generated by a liquid injection into the bag.

8.2.5.1 Obtain spiking stock that is sufficiently concentrated to spike a Tedlar® sample without exceeding the 1% volume limit. Select appropriate analytes, analyte homologs, or isotopically labeled analogs in cylinders or SUMMA® canisters for gaseous injections or neat liquids or methanol solutions for liquid injections.

8.2.5.2 Install an injection port that consists of a Swagelok® tee fitting with a septum in the sample line just before the 1/4-in. Quick connector on the Tedlar® bag (Figure 1). Locate this port as close to the bag as possible to minimize wall effects. Use a new septum for each sampling run that involves spiking.

8.2.5.3 Perform a leak test as described in Sec. 7.3 with the injection port in line.

8.2.5.4 Start sampling the stack as described in Secs. 7.4 and 7.5.

8.2.5.5 In preparation for injection, clean the syringe by flushing three times with an inert gas (high purity N_2, 99.998%) for gaseous injections, or with methanol for liquid injections. Then flush the syringe three times with the gaseous or liquid spiking standard.

8.2.5.6 After half an hour of sample collection, take up the desired volume of the spiking standard into the syringe (for gases, allow the standard to equilibrate to atmospheric pressure) and inject it through the septum into the bag without interrupting the sampling procedure. All apparatus upstream of the bag should be under slight negative pressure.

8.3 An EPA performance audit shall be completed during a trial burn as a check on the entire Tedlar® bag sampling system. The audit results should agree within 50% to 150% of the expected value for each specific compound of interest. This audit consists of collecting a gas sample containing one or more volatile organic compounds in the Tedlar® bag sampling system from an EPA audit gas cylinder. Collection of the audit sample in the Tedlar® bag sampling system may be conducted either in the laboratory or at the field test site. Analysis of the Tedlar® bag audit sample must be by the same person, at the same time, and with the same analytical procedure as used for the regular Tedlar® bag samples from the field test.

8.4 Evaluation of analytical procedures for a selected series of compounds shall include the sample preparation procedures and each associated analytical determination. Challenge the analytical procedures by spiking the test compounds at appropriate levels carried through the procedures.

8.5 Determine the overall method detection limits (lower and upper) on a compound-by-compound basis according to the 40 CFR Part 136b for the determination of the detection limit. Different compounds may exhibit different collection efficiencies as well as instrumental minimum detection limit.

8.6 During the sampling planning stage, determine whether each compound on the analyte list has been validated for this method at a similar source. For all compounds which have not, either plan to determine the method precision and bias by dynamic spiking ahead of the filter in accordance with Method 301 (Reference 6) or present a justification for not running Method 301 to appropriate regulatory personnel. The justification may be based on previous validation of one or more compounds very similar to those in question, or on other technical issues as appropriate.

9.0 METHOD PERFORMANCE

Method evaluation data are available from testing at a coal-fired power plant (Reference 10). Compounds which met method validation criteria are shown in Sec. 1; compounds which were tested and failed to meet method validation criteria are also shown in Sec. 1.

10.0 REFERENCES

1. Howe, G.B., B.A. Pate, and R.K.M. Jayanty, "Stability of Volatile Principal Organic Hazardous Constituents (POHCs) in Tedlar® Bags", Research Triangle Institute Report to the EPA, Contract No. 68-02-4550, 1991.

2. Andino, J.M., and J.W. Butler, "A Study of the Stability of Methanol-Fueled Vehicle Emissions in Tedlar® Bags", *Environ. Sci. Technol.* 1991, 25(9), 1644-1646.

3. Posner, J.C., and W.J. Woodfin, "Sampling with Gas Bags I: Loses of Analyte with Time", Appendix L Industrial Hygiene, 1986, (4), 163-168.

4. Seila, R.L., W.A. Lonneman, and S.A. Meeks, "Evaluation of Polyvinyl Fluoride as a Container Material for Air Pollution Samples", J. Environ. Sci. Health., 1976, 2, 121-130.

5. U.S. Environmental Protection Agency, Hazardous Waste Incineration Measurement Guidance Manual, Volume III of the Hazardous Waste Incineration Guidance Series, EPA/625/6-89/021.

6. U.S. Environmental Protection Agency, Method 301, "Protocol for the Field Validation of Emission Concentrations from Stationary Sources", EPA 450/4-90-015, February 1991.

7. 40 CFR Part 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit".

8. Kanniganti, R., Moreno, R.L., and J.T. Bursey, Radian Corporation, Research Triangle Park, North Carolina, "Method 0040: Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags", EPA Contract No. 68-D1-0010.

9. 40 CFR Part 60, Appendix A, Methods 1, 2, 3, 4, 5, 18 and 25.

10. U. S. Environmental Protection Agency, Contract No. 68-D4-0022, Work Assignment 34 to Eastern Research Group, Incorporated, “Field Evaluation of EPA Method 0040 (Volatiles Using Bags) at a Coal-Fired Power Plant,” September 30, 1996.

TABLE 1

COMPOUNDS FOR WHICH APPLICABILITY OF THE METHOD HAS BEEN DEMONSTRATED

Compound	CAS No.	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Instrument Detection Limit[a] (ppm)
Dichlorodifluoromethane	75-71-8	-30	Gas	0.20
Vinyl chloride	75-01-4	-19	Gas	0.11
1,3-Butadiene	106-99-0	-4	Gas	0.90
1,2-Dichlor-1,1,2,2-tetrafluoroethane	76-14-2	4	Gas	0.14
Methyl bromide	74-83-9	4	Gas	0.14
Trichlorofluoromethane	353-54-8	24	88	0.18
1,1-Dichloroethene	75354	31	22	0.07
Methylene chloride	75-09-2	40	44	0.05
1,1,2-Trichlorotrifluoroethane	76-13-1	48	37	0.13
Chloroform	67-66-3	61	21	0.04
1,1,1-Trichloroethane	71-55-6	75	13	0.03
Carbon tetrachloride	56-23-5	77	11	0.03
Benzene	71-43-2	80	10	0.16
Trichloroethene	79-01-6	87	8	0.04
1,2-Dichloropropane	78-87-5	96	5	0.05
Toluene	108-88-3	111	3	0.08
Tetrachloroethylene	127-18-4	121	2	0.03

[a]Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits

TABLE 2

PROBLEMS THAT CAN INVALIDATE TEDLAR® BAG SAMPLING
DATA AND SUGGESTED REMEDIES

Problem	Remedy
1. Condensation of the gases or water vapor in the bag	Sample below the condensation point of the analytes; lower the temperature in the condensate trap.
2. Leaks developing in the bag during testing, transport, and/or analysis	Use double sealed bags; perform additional sampling runs; protect the bags from sharp objects by sampling and shipping in rigid, opaque containers; ship the bags in the same containers used during sampling.
3. Hydrocarbon contamination	Minimize exposure of the bag to heat and direct light, by sampling and shipping in rigid, opaque containers; purge the bags with ultrapure N_2 in the laboratory and establish through analysis that the hydrocarbon levels are acceptable; use the bags only once.

FIGURE 1
SCHEMATIC OF THE METHOD 0040 SAMPLING TRAIN

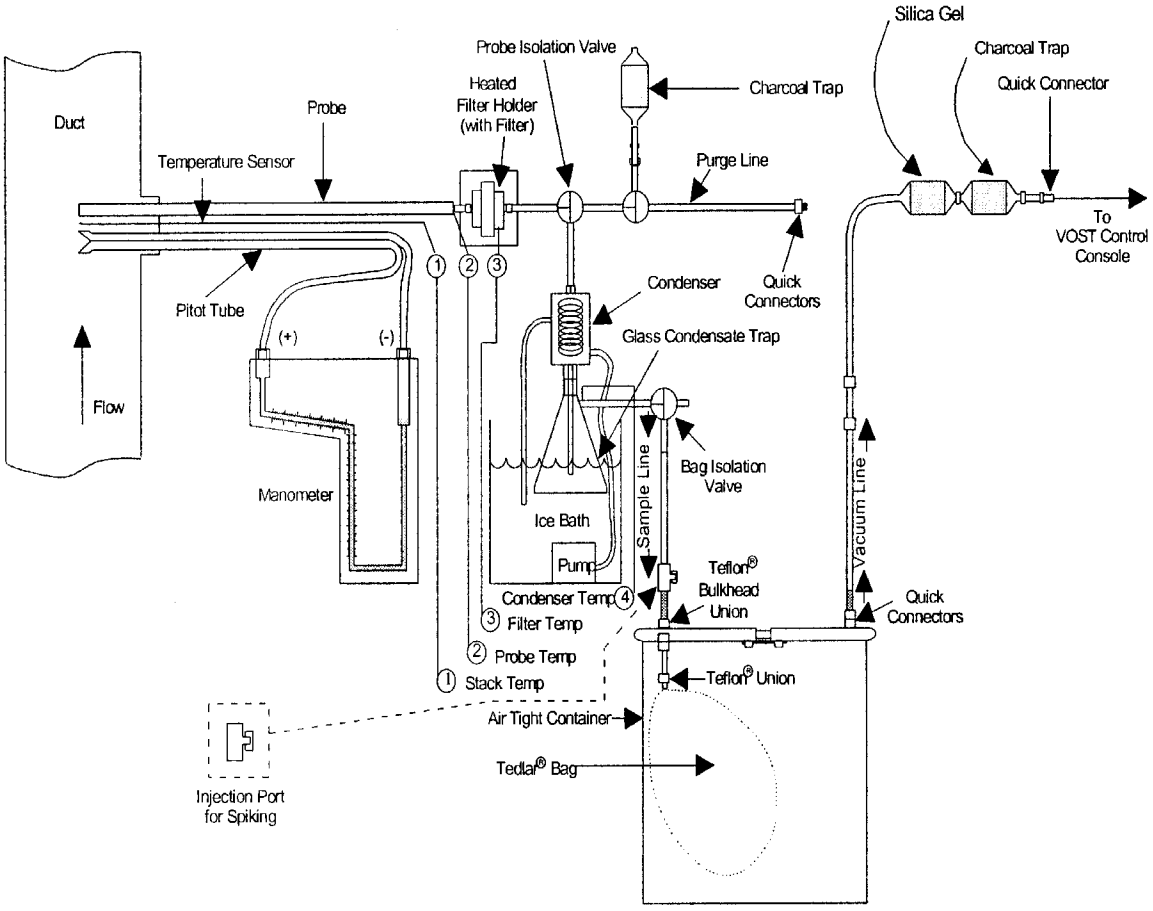


FIGURE 2
ISOLATION VALVE DESIGN

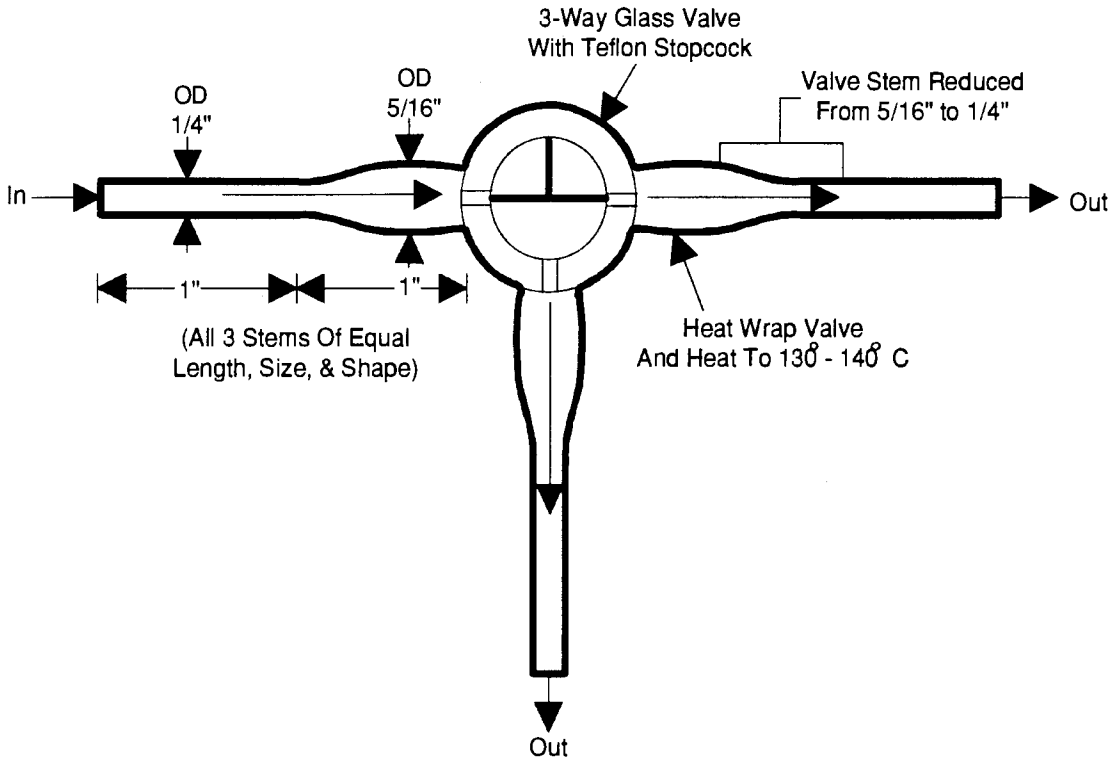
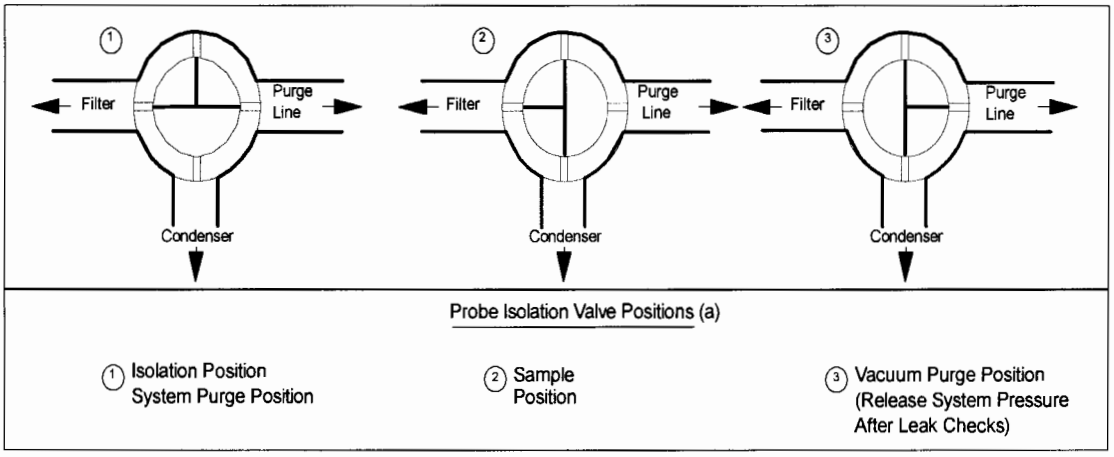
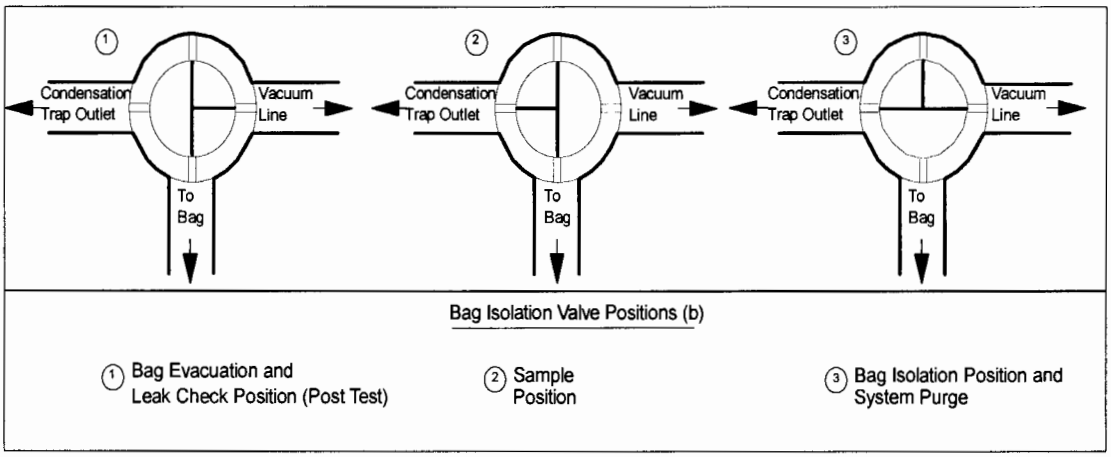


FIGURE 3
VALVE OPERATION





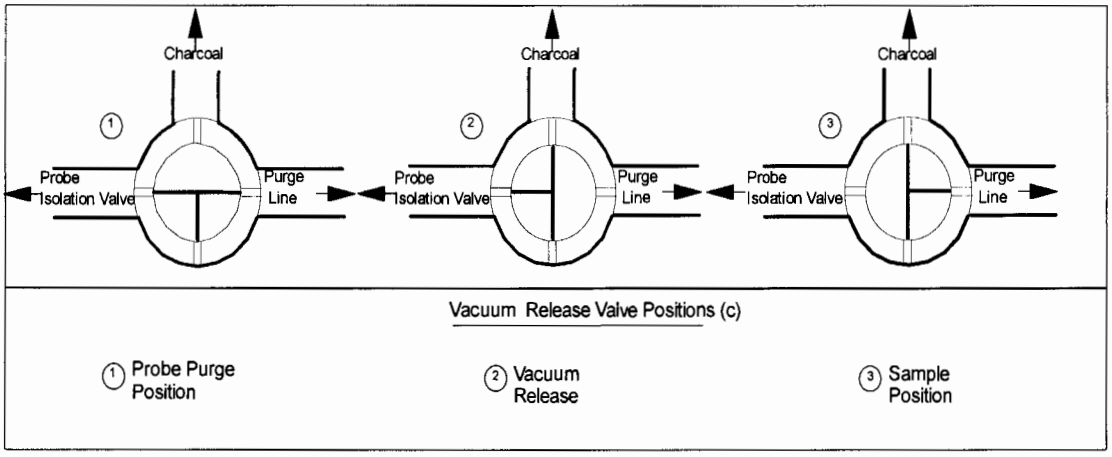


FIGURE 4
DIAGRAM OF CONTROL CONSOLE

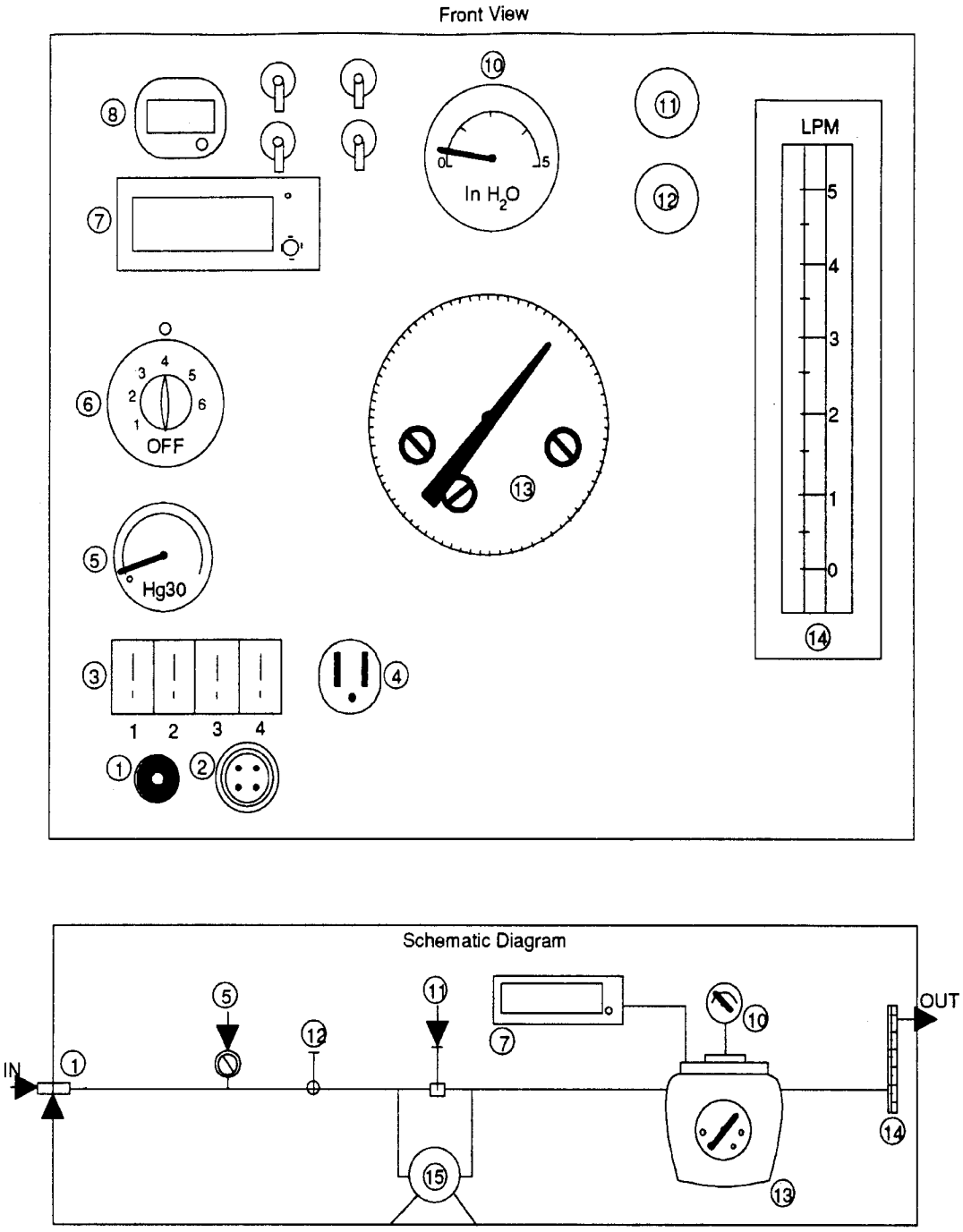


FIGURE 4 (Continued)
CONTROL CONSOLE COMPONENTS

1. 1/4 in. S.S. Quick Connect - Vacuum line inlet from sample train (to bag container).

2. Amphenol Receptacle - provides power through umbilical to probe heat & water pump.

3. Thermocouple Receptacles - 4 thermocouple inlets for:
    1. Stack Temperature
    2. Probe Temperature
    3. Condenser Temperature
    4. Ambient Temperature

4. 110 VAC Receptacle - auxiliary power for isolation valve heat.

5. Vacuum Gauge - 0-30 in. Hg.

6. Heat Controller

7. Digital Thermocouple Read Out - 10 channel (displays temperature readings during sampling)
    - (1-4 remote as listed above)
    - (5 dry gas meter temperature)
    - (6-10 spares)

8. Timer (optional)

9. Power Switches - control (on/off)
    1. Main power - with separate switches for each.
    2. Sample pump
    3. Water pump
    4. Timer

10. Meter pressure Gauge - (inches water column)

11. Fine Adjustment (Bypass) Valve

12. Coarse Adjustment (on/off) Valve

13. Dry Gas Meter

14. Rotometer (Flow Meter)

15. Pump

FIGURE 5
PRETEST SURVEY DATA FORM

1. Name of Company _____ Date _____

Address _____

_____

_____

Contacts _____

Phone Numbers _____

Process to be sampled _____

_____

Duct or vent to be sampled _____

_____

II. Process description _____

_____

Raw Material _____

_____

Products _____

_____

Operating cycle

Check: Batch _____Continuous _____ Cyclic _____

Timing of batch or cycle _____

Best time to test _____

III. Sampling site

A. Description

Site description _____

Duct shape and size _____

Materials _____

Wall thickness _____inches

Upstream distance _____ inches _____diameter

Downstream distance _____ inches _____diameter

Size of port _____

FIGURE 5 (Continued)

Temperature _____ °C Data Source _____

Velocity _____ Data Source _____

Static pressure _____ inches H_2O Data Source _____

Moisture content _____% Data Source _____

Particulate content _____ Data Source _____

Gaseous components

N_2	_____%	Hydrocarbons	_____ ppm
O_2	_____%	_____	_____ ppm
CO	_____%	_____	_____ ppm
CO_2	_____%	_____	_____ ppm
SO_2	_____%	_____	_____ ppm

Hydrocarbon components

_____	_____ ppm
_____	_____ ppm
_____	_____ ppm
_____	_____ ppm
_____	_____ ppm
_____	_____ ppm

B. Sampling considerations

Location to set up GC _____

_____

Power available at duct _____

_____

Plant entry requirements _____

_____

Security agreements _____

_____

Potential problems _____

_____

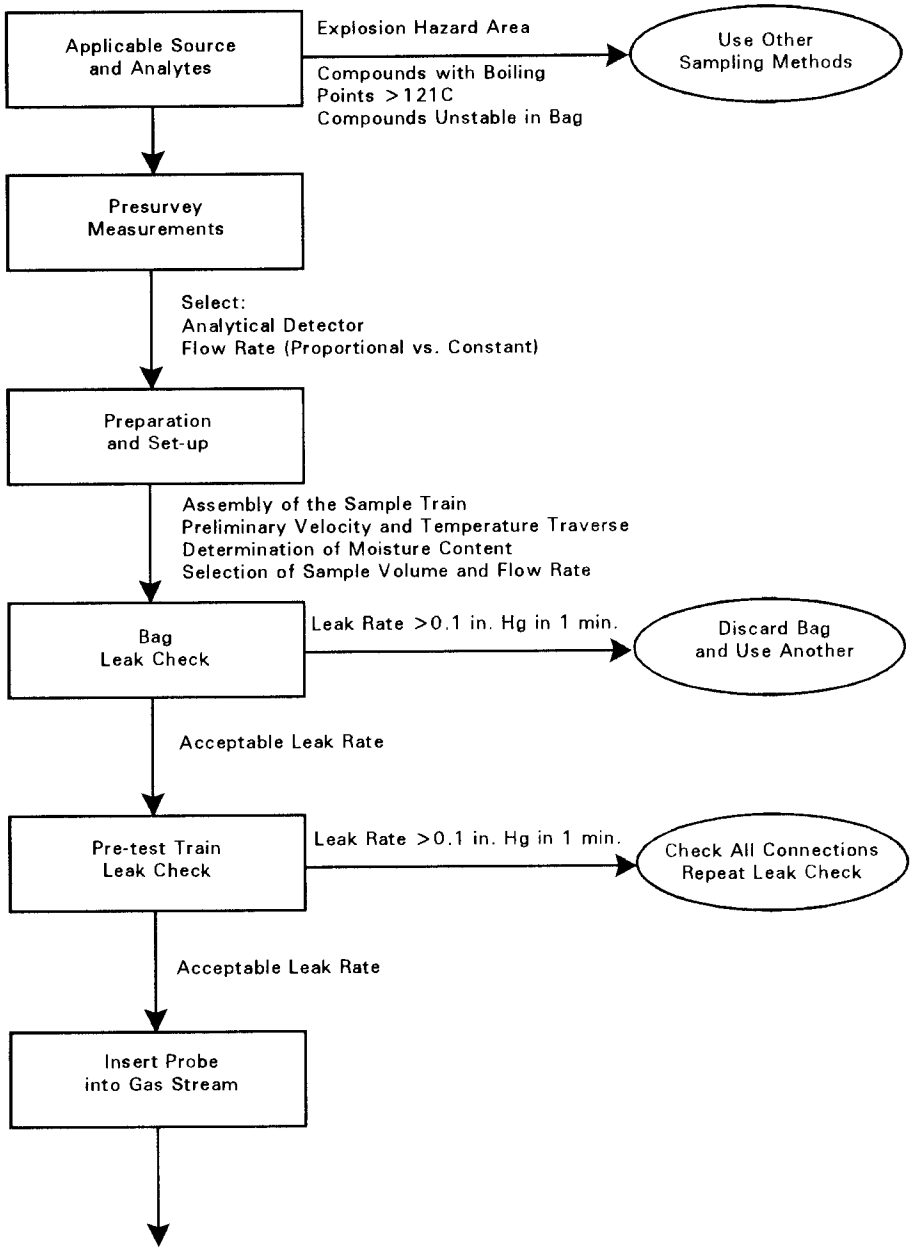
Site diagrams (Attach additional sheets if required).

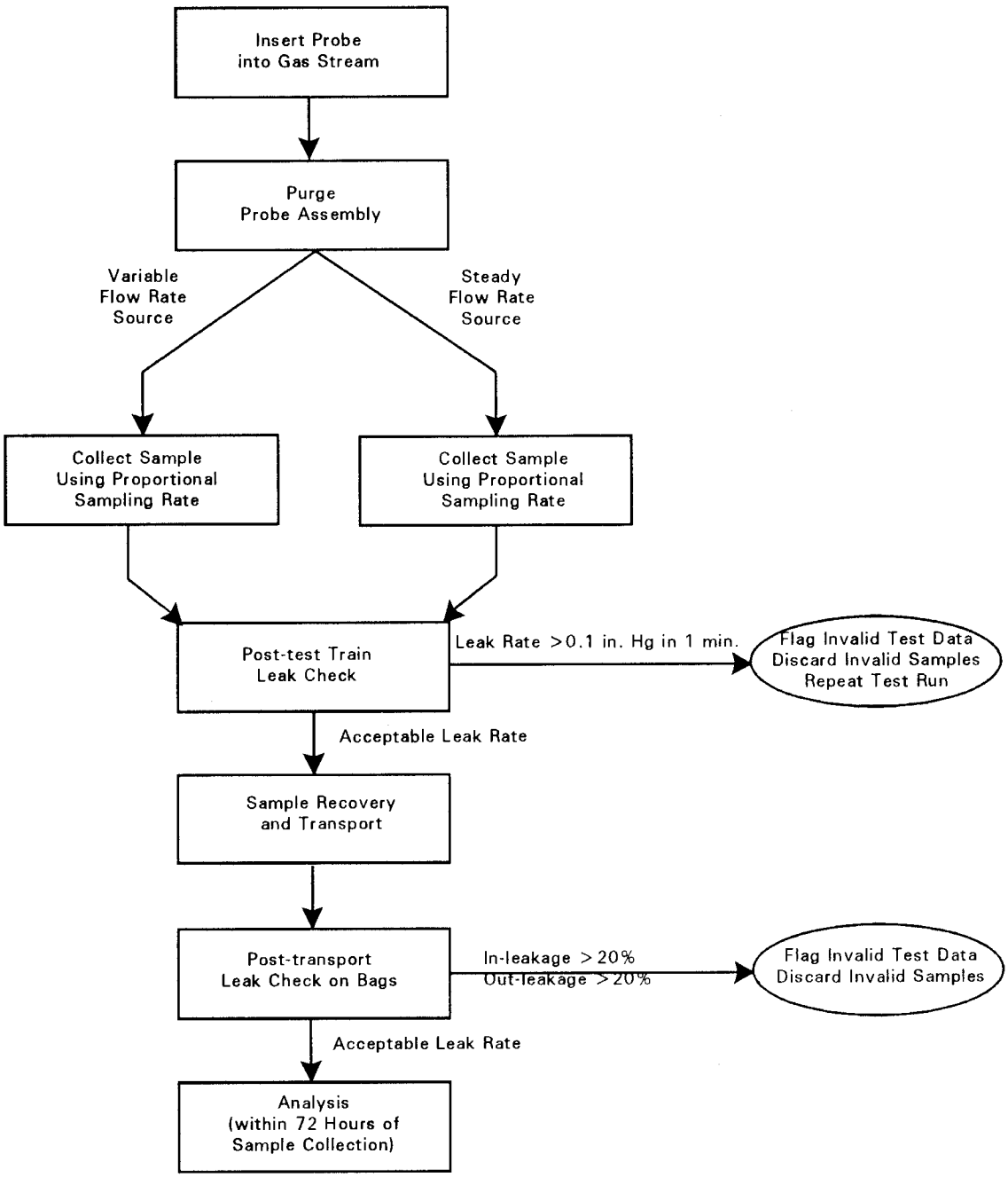
FIGURE 6
FIELD SAMPLING DATA FORM

Plant	_____	Dilution system: (dynamic)	_____
City	_____	emission flowsetting	_____
Operator	_____	diluent flowsetting	_____ (in. Hg)
Date	_____	Dilution system (statis)	_____
Run number	_____	emission flowsetting	_____
Stack dia. (in.)	_____	Final Leak Check	_____ (cfm)
Sample box number	_____	Vacuum during leak check	_____ (in. H_2O)
Pitot tube (C_p)	_____	Sampling point location	_____
Static press	_____ (in. H_2O)	Total condensate volume	_____ mL
Flowmeter calib (Y)	_____	VOA vial size	_____ mL
Average (ΔP)	_____ (in. H_2O)	VOA vial number	_____
Initial flowmeter setting	_____	Tedlar® bag volume	_____ liters
Average stack temperature	_____ °C	Container volume	_____ liters
Barometric pressure	_____	Container number	_____

FIGURE 6 (Continued)

Sampling, time, min.	Clock time, 24 hr.	Velocity head (in.) (H_2O) (ΔP)	Flowmeter setting (ft^3/min)	Temperature Readings			
				Stack (°C)	Probe (°C)	Sample Line (°C)	Flowmeter Box (°C)
Total		Avg	Avg	Avg	Avg	Avg	Avg


Applicable Source and Analytes
Explosion Hazard Area
Compounds with Boiling Points >121C
Compounds Unstable in Bag
Use Other Sampling Methods
Presurvey Measurements
Select:
Analytical Detector
Flow Rate (Proportional vs. Constant)
Preparation and Set-up
Assembly of the Sample Train
Preliminary Velocity and Temperature Traverse
Determination of Moisture Content
Selection of Sample Volume and Flow Rate
Bag Leak Check
Leak Rate >0.1 in. Hg in 1 min.
Discard Bag and Use Another
Acceptable Leak Rate
Pre-test Train Leak Check
Leak Rate >0.1 in. Hg in 1 min.
Check All Connections Repeat Leak Check
Acceptable Leak Rate
Insert Probe into Gas Stream


Insert Probe into Gas Stream
Purge Probe Assembly
Variable Flow Rate Source
Steady Flow Rate Source
Collect Sample Using Proportional Sampling Rate
Collect Sample Using Proportional Sampling Rate
Post-test Train Leak Check
Leak Rate >0.1 in. Hg in 1 min.
Flag Invalid Test Data
Discard Invalid Samples
Repeat Test Run
Acceptable Leak Rate
Sample Recovery and Transport
Post-transport Leak Check on Bags
In-leakage >20%
Out-leakage >20%
Flag Invalid Test Data
Discard Invalid Samples
Acceptable Leak Rate
Analysis (within 72 Hours of Sample Collection)

METHOD 0050

ISOKINETIC HCl/Cl_2 EMISSION SAMPLING TRAIN

1.0 SCOPE AND APPLICATION

1.1 This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl_2, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators and municipal waste combustors. The collected samples are analyzed using Method 9057. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (e.g., HCl dissolved in water droplets). A midget impinger train sampling method designed for sampling sources of HCl/Cl_2 emissions not in particulate form is presented in Method 0051. The method has potential for collection of all halogens and halogen acids, but has not yet been fully evaluated for that use. For analytical determination of additional halides, Method 9056 is used, rather than Method 9057.

1.2 This method is not acceptable for demonstrating compliance with HCl emission standards less than 20 ppm.

1.3 This method may also be used to collect samples for subsequent determination of particulate emissions (Method 5, see Ref. 1) following the additional sampling procedures described.

2.0 SUMMARY OF METHOD

2.1 Gaseous and particulate pollutants are withdrawn from an emission source and are collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain liquid droplets. The Teflon mat or quartz-fiber filter collects other particulate matter including chloride salts. Acidic and alkaline absorbing solutions collect gaseous HCl and Cl_2, respectively. Following sampling of emissions containing liquid droplets, any HCl/Cl_2 dissolved in the liquid in the cyclone and/or on the filter is vaporized to gas and ultimately collected in the impingers by pulling Ascarite II^R conditioned ambient air through the sampling train. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride (Cl^-) ions. The Cl_2 gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^-, and hypochlorous acid (HClO). The (Cl^-) ions in the separate solutions are measured by ion chromatography (Method 9057). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in Method 5.

2.2 The stoichiometry of HCl and Cl_2 collection in the sampling train is as follows: In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl^-) according to the following formula:

$$HCl + H_2O = H_3O^+ + Cl^-$$

The Cl_2 gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^-, and hypochlorous acid (HClO) as shown:

$$H_2O + Cl_2 = H^+ + Cl^- + HClO$$

Sodium thiosulfate solution is added to the contents of the hydroxide filled impingers, in order to promote the following reaction.

$$S_2O_3^{-2} + 4OCl^- + 2OH^- = 2SO_4^{-2} + 4Cl^- + H_2O$$

Conversion of all the original Cl_2 to the stable Cl^- ion, and appropriate adjustment of the analysis calculations, removes the possibility of partial reduction of OCl^- to Cl^- and the resulting high bias to the results.

3.0 INTERFERENCES

3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl_2) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl_2 gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present.

4.0 APPARATUS AND MATERIALS

4.1 Sampling Train.

4.1.1 A schematic of the sampling train used in this method is shown in Figure 1. This sampling train configuration is adapted from Method 5 and Method 0010 procedures, and, as such, the majority of the required equipment is identical to that used in Method 0010 determinations. The new components required are a glass nozzle and probe, a Teflon union, a quartz-fiber or Teflon mat filter (see Section 5.5), a Teflon frit, and acidic and alkaline absorbing solutions.

4.1.2 Construction details for the basic train components are provided in Section 3.4 of EPA's Quality Assurance Handbook, Volume III (Reference 2); commercial models of this equipment are also available. Additionally, the following subsections identify allowable train configuration modifications.

4.1.3 Basic operating and maintenance procedures for the sampling train are also described in Reference 2. As correct usage is important in obtaining valid results, all users should refer to Reference 2 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

4.1.3.1 Probe nozzle. Glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant I.D. The nozzle shall be buttonhook or elbow design. The nozzle should be coupled to the probe liner using a Teflon union. It is recommended that a stainless steel nut be used on this union. In cases where the stack temperature exceeds 210°C (410°F), a one-piece glass nozzle/liner assembly must be used. A range of nozzle sizes suitable for isokinetic sampling should be available. Each nozzle shall be calibrated according to the procedures outlined in Method 5.

4.1.3.2 Probe liner. Borosilicate or quartz-glass tubing with a heated system capable of maintaining a gas temperature of 120 ± 14°C (248 ± 25°F) at the exit end during sampling. Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed and calibrated according to the procedure in Reference 2 are considered acceptable. Either borosilicate or quartz-glass probe liners may be used for stack temperatures up to about 480°C (900°F). Quartz liners shall be used for temperatures between 480 and 900°C (900 and 1650°F). (The softening temperature for borosilicate is 820°C (1508°F), and for quartz 1500°C (2732°F).) Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500°C.

4.1.3.3 Pitot tube. Type S, as described in Section 2.1 of Method 2 (Reference 1). The pitot tube shall be attached to the probe to allow constant monitoring of the stack-gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Section 3.1.1 of Reference 2) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 3.1.1 of Reference 2.

4.1.3.4 Differential pressure gauge. Inclined manometer or equivalent device as described in Section 2.2 of Method 2. One manometer shall be used for velocity-head (delta P) readings and the other for orifice differential pressure (delta H) readings.

4.1.3.5 Cyclone (optional), glass.

4.1.3.6 Filter holder. Borosilicate glass, with a Teflon frit filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone.

4.1.3.7 Filter heating system. Any heating system capable of maintaining a temperature of 120 ± 14°C (248 ± 25°F) around the filter holder and cyclone during sampling. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

4.1.3.8 Impinger train. The following system shall be used to determine the stack gas moisture content and to collect HCl and Cl_2: five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first impinger shown in Figure 1 (knockout or condensate impinger) is optional and is recommended as a water knockout trap for use under test conditions which require such a trap. If used, this impinger should be constructed as described below for the alkaline impingers, but with a shortened stem, and should contain 50 ml of 0.05 M H_2SO_4. The following two impingers (acid impingers which each contain 100 ml of 0.05 M H_2SO_4) shall be of the Greenburg-Smith design with the standard tip (see Method 0010, Section 4). The next two impingers (alkaline impingers which each contain 100 mL of 0.1 M NaOH) and the last impinger (containing silica gel) shall be of the Greenburg-Smith design modified

by replacing the tip with a 1.3-cm (½-in.) I.D. glass tube extending about 1.3 cm (½ in.) from the bottom of the impinger (see Method 5, Section 4).

The condensate, acid, and alkaline impingers shall contain known quantities of the appropriate absorbing reagents. The last impinger shall contain a known weight of silica gel or equivalent desiccant.

4.1.3.9 Metering system. The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1%, an orifice meter (rate meter), and related equipment, as shown in Figure 1. At a minimum, the pump should be capable of 113 m^3/min (4 cfm) free flow, and the dry-gas meter should have a recording capacity of 0-28.3 m^3 (0-999.9 ft^3) with a resolution of 0.142 liters (0.005 ft^3). Other metering systems capable of maintaining sampling rates within 10% of isokineticity and of determining sample volumes to within 2% may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

4.1.3.10 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30-m (100 ft) elevation increase (vice versa for elevation decrease).

4.1.3.11 Gas density determination equipment. Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of Method 2), and gas analyzer, if necessary (as described in Method 3, Reference 1). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-7). As a second alternative, if the stack gas is saturated, the stack temperature may be measured at a single point near the center of the stack.

4.1.3.12 Ascarite tube for conditioning ambient air. Tube tightly packed with approximately 150 g of fresh 8 to 20 mesh Ascarite II^R sodium hydroxide coated silica, or equivalent, to dry and remove acid gases from the ambient air used to remove moisture from the filter and optional cyclone. The inlet and outlet ends of the tube should be packed with at least 1 cm thickness of glass wool or filter material suitable to prevent escape of Ascarite II fines. Fit one end with flexible tubing, etc. to allow connection to probe nozzle.

4.2 Sample Recovery.

4.2.1 Probe liner. Probe and nozzle brushes; nylon (Teflon) bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner and the probe nozzle.

4.2.2 Wash bottles. Two. Polyethylene or glass, 500 mL or larger.

4.2.3 Glass sample storage containers. Glass, 500- or 1,000-mL. Screw-cap liners shall be Teflon and constructed so as to be leak-free. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

4.2.4 Petri dishes. Glass or plastic sealed around the circumference with Teflon tape, for storage and transport of filter samples.

4.2.5 Graduated cylinder and/or balances. To measure condensed water to the nearest 1 mL or 1 g. Graduated cylinders shall have subdivisions not >2 mL. Laboratory triple-beam balances capable of weighing to ± 0.5 g or better are required.

4.2.6 Plastic storage containers. Screw-cap polypropylene or polyethylene containers to store silica gel.

4.2.7 Funnel and rubber policeman. To aid in transfer of silica gel to container (not necessary if silica gel is weighed in field).

4.2.8 Funnels. Glass, to aid in sample recovery.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in the method refer to reagent grade water as defined in Chapter One unless otherwise specified. It is advisable to analyze a blank sample of this water prior to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values.

5.3 Sulfuric acid (0.05 M), H_2SO_4. Used as the HCl absorbing reagent in the impinger train. To prepare 1 L, slowly add 2.80 mL of concentrated H_2SO_4 to about 900 mL of water while stirring, and adjust the final volume to 1-L using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values.

5.4 Sodium hydroxide (0.1 M), NaOH. Used as the Cl_2 absorbing reagent in the impinger train. To prepare 1 L, dissolve 4.00 g of solid NaOH in about 900 mL of water and adjust the final

volume to 1-L using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values.

5.5 Filter. Quartz-fiber or Teflon mat (e.g., Pallflex^{R} TX40HI45) filter, or equivalent.

5.6 Silica gel. Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants may be used if equivalence can be demonstrated.

5.7 Acetone. When using this train for determination of particulate emissions, reagent grade acetone, ≤ 0.001 percent residue, in glass bottles is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤ 0.001 percent) shall be used. In no case shall a blank value greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

5.8 Crushed ice. Quantities ranging from 10-50 lb may be necessary during a sampling run, depending on ambient air temperature.

5.9 Screw-on connectors, Teflon sleeves on ground-glass joints, or other greaseless fittings should be used.

5.10 Sodium thiosulfate (0.5 M), $Na_2S_2O_3$. Used as the reducing agent added to the sodium hydroxide filled impingers to promote the reaction given in Section 2.0. Buy premixed reagent grade, as free of chloride as possible.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection is described in this method. The analytical procedures for HCl and Cl_2 are described in Method 9057 and for particulate matter in Method 0100.

6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

7.0 PROCEDURE

7.1 Preparation for Field Test.

7.1.1 All sampling equipment shall be maintained and calibrated the procedures described in Section 3.4.2 of EPA's Quality Assurance Handbook, Volume III (Reference 2) and in Methods 1-5 (Reference 1).

7.1.2 Weigh several 200-300-g portions of silica gel in airtight containers to the nearest 0.5-g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger just prior to train assembly.

7.1.3 Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass or plastic Petri dishes) and keep the filters in these containers at all times except during sampling (and weighing for particulate analysis).

7.1.4 If a particulate determination will be conducted, desiccate the filters at 20 ± 5.6°C (68 ± 10°F) and ambient pressure for at least 24 h, and weigh at intervals of at least 6 h to a constant weight (i.e., <0.5-mg change from previous weighing), recording results to the nearest 0.1 mg. During each weighing, the filter must not be exposed for more than a 2-min period to the laboratory atmosphere and relative humidity above 50%. Alternatively, the filters may be oven-dried at 105°C (220°F) for 2-3 h, desiccated for 2 h, and weighed.

7.2 Preliminary Field Determinations.

7.2.1 Select the sampling site and the minimum number of sampling points according to Method 1. Determine the stack pressure, temperature, and range of velocity heads using Method 2. It is recommended that a leak-check of the pitot lines (see Method 2) be performed. Determine the stack-gas moisture content using Method 4 or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3. If integrated Method 3 (Reference 1) sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as the sample run.

7.2.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2 of Method 2).

7.2.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

7.2.4 The total sampling time should be two hours. Allocate the same time to all traverse points defined by Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min. Size the condensate impinger for the expected moisture catch or be prepared to empty it during the run.

7.3 Preparation of Sampling Train.

7.3.1 Add 50 mL of 0.05 M H_2SO_4 to the condensate impinger, if used. Place 100 mL of 0.05 M H_2SO_4 in each of the next two impingers. Place 100 mL of 0.1 M NaOH in each of the following two impingers. It is essential that the NaOH filled impingers be maintained strongly basic throughout the sampling run. In highly acid stack environments, this may require measures such as stronger base, more volume of basic solution, or changeout of impinger liquid during the run. When in doubt, the pH of the solution should be monitored frequently or continuously. Finally, transfer approximately 200-300 g of preweighed silica gel from its container to the last impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger

during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

7.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) filter (weighed, if particulate matter is to be determined) in the filter holder. Be sure that the filter is properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

7.3.3 To use glass liners, install the selected nozzle using a Viton-A O-ring when stack temperatures are <260°C (500°F) and a woven glass fiber gasket when temperatures are higher. Other connecting systems utilizing Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

7.3.4 Set up the train as in Figure 1. Connect temperature sensors to the appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

7.3.5 Place crushed ice around the impingers.

7.3.6 Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

7.4 Leak-check Procedures.

7.4.1 Pretest leak-check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

7.4.1.1 If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380-mm Hg (15-in. Hg) vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

7.4.1.2 If a woven glass fiber gasket is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the cyclone, if used, or the filter holder and pulling a 380-mm Hg (15-in. Hg) vacuum (see NOTE above). Then, connect the probe to the train and leak-check at about 25-mm Hg (1-in. Hg) vacuum; alternatively, leak-check the probe with the rest of the sampling train in one step at 380-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4% of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

7.4.1.3 The following leak-check instructions for the sampling train may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of the

bypass valve; this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

7.4.1.4 When the leak-check is completed, first slowly remove the plug from the inlet to the probe, cyclone, or filter holder and immediately turn off the vacuum pump. This prevents the liquid in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the fifth impinger.

7.4.2 Leak-checks during sample run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary or a port change is conducted, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be conducted according to the procedure outlined in Section 7.4.1, except that it shall be conducted at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester shall void the sampling run. Immediately after a component change or port change, and before sampling is reinitiated, another leak-check similar to a pre-test leak-check is recommended.

7.4.3 Post-test leak-check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done using the same procedures as those with the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester shall void the sampling run.

7.5 Train Operation.

7.5.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic. Maintain a temperature around the filter and (cyclone, if used) of 120 ± 14°C (248 ± 25°F).

7.5.2 For each run, record the data required on a data sheet such as the one shown in Figure 2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings required by Figure 2 at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

7.5.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are positioned properly. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to

isokinetic conditions using a calculator or a nomograph. Nomographs are designed for use when the Type S pitot tube coefficient is 0.84 and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations (see Reference 3).

7.5.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack, to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

7.5.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

7.5.6 Traverse the stack cross section, as required by Method 1, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

7.5.7 During the test run, make periodic adjustments to keep the temperature around the filter holder (and cyclone, if used) at the proper level. Add more ice, and, if necessary, salt to maintain a temperature of <20°C (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

7.5.8 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, it may be replaced in the midst of a sample run. Using another complete filter holder assembly is recommended, rather than attempting to change the filter itself. After a new filter assembly is installed, conduct a leak-check. If determined, the total particulate weight shall include the summation of all filter assembly catches.

7.5.9 If the condensate impinger becomes too full, it may be emptied, recharged with 50 mL of 0.05 M H_2SO_4, and replaced during the sample run. The condensate emptied must be saved and included in the measurement of the volume of moisture collected and included in the sample for analysis. The additional 50 mL of absorbing reagent must also be considered in calculating the moisture. After the impinger is reinstalled in the train, conduct a leak-check.

7.5.10 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains.

7.5.11 Note that when two or more trains are used, separate analyses of the particulate catch (if applicable) and the HCl and Cl_2 impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In that case, the particulate catch and the HCl and Cl_2 impinger catches from the individual trains may be combined, and a single particulate analysis and single HCl and Cl_2 analyses of the impinger contents may be performed.

7.5.12 At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading.

7.5.13 If there is any possibility that liquid has collected in the glass cyclone and/or on the filter, connect the Ascarite tube at the probe inlet and operate the train with the filter heating system at 120 ± 14°C (248 ± 25°F) at a low flow rate (e.g., $\Delta H = 1$) sufficient to vaporize the liquid and purge any HCl in the cyclone or on the filter and pull it through the train into the impingers. After 30 minutes, turn off the flow, remove the Ascarite tube, and examine the cyclone and filter for any visible moisture. If moisture is visible, repeat this step for 15 minutes. A 45 minute cyclone purge is not effective for removing greater than 25 mL of solution from the cyclone. Also, a 45 minute purge is more effective when the filter and probe temperatures are increased to 177°C. (See "Laboratory Evaluation of Method 0050 for Hydrogen Chloride").

7.5.14 Conduct a post-test leak-check. Also, leak-check the pitot lines as described in Method 2. The lines must pass this leak-check in order to validate the velocity-head data.

7.5.15 If the moisture value is available, calculate percent isokineticity (see Section 7.7.10) to determine whether the run was valid or another test run should be conducted.

7.6 Sample Recovery

7.6.1 Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap over the tip. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the holder.

7.6.2 Before moving the sampling train to the cleanup site, remove the probe and cap the open outlet, being careful not to lose any condensate that might be present. Cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at the filter holder and let any condensed water drain into the first impinger. Cap the filter holder outlet and the impinger inlet. Ground glass stoppers, plastic caps, serum caps, Teflon tape, Parafilm^{R}, or aluminum foil may be used to close these openings.

7.6.3 Transfer the probe and filter/impinger assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

7.6.4 Save portions of all washing solutions used for cleanup (acetone and reagent grade water) and the absorbing reagents (0.05 M H_2SO_4 and 0.1 M NaOH) as blanks. Transfer 200 mL of each solution directly from the wash bottle being used (rinse solutions) or the supply container (absorbing reagents) and place each in a separate, prelabeled glass sample container.

7.6.5 Inspect the train prior to and during disassembly and note any abnormal conditions.

7.6.6 Container No. 1 (filter catch for particulate determination). Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use one or more pair of tweezers to handle the filter. If it is necessary to fold the filter, ensure that the particulate cake is inside the fold. Carefully transfer to the Petri dish any particulate matter or filter fibers that adhere to the filter holder gasket, using a dry nylon bristle brush or sharp-edged blade, or both. Label the container and seal with Teflon tape around the circumference of the lid.

7.6.7 Container No. 2 (front-half rinse for particulate determination). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone into a glass container. Retain an acetone blank and analyze with the samples.

7.6.8 Perform rinses as follows: carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particles; then make a final rinse of the inside surface with the acetone. Brush and rinse the inside parts of the Swagelok fitting with the acetone in a similar way until no visible particles remain.

7.6.9 Have two people rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with solvent. Let the acetone drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washed to the container.

7.6.10 Follow the acetone rinse with a probe brush. Hold the probe in an inclined position and squirt acetone into the upper end while pushing the probe brush through the probe with a twisting action; place a sample container underneath the lower end of the probe and catch any acetone and particulate matter that is brushed from the probe. Run the brush through the probe three or more times until no visible particulate matter is carried out with the acetone or none remains in the probe liner on visual inspection. Rinse the brush with acetone and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above. Between sampling runs, keep brushes clean and protected from contamination.

7.6.11 Clean the inside of the front half of the filter holder and cyclone by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times, or more if needed, to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if applicable). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all rinses and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents.

7.6.12 Container No. 3 (knockout and acid impinger catch for moisture and HCl determination). Disconnect the impingers. Measure the liquid in the acid and knockout impingers to within ± 1 mL by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This

information is required to calculate the moisture content of the emission gas. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers and the connecting glassware (and tubing, if used) with water, and add these rinses to the storage container. Seal the container, shake to mix, and label. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Retain rinse water and acidic absorbing solution blanks and analyze with the samples.

7.6.13 Container No. 4 (alkaline impinger catch for Cl_2 and moisture determination). Measure and record the liquid in the alkaline impingers as described in Section 7.6.12. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Add 2 mL or more of 0.5 M $Na_2S_2O_3$. to the sodium hydroxide (Cl_2) samples. It is necessary to add sufficient $Na_2S_2O_3$ to reduce the OCl^-, but too much thiosulfate may interfere with the ion chromatography analysis. The amount needed will vary with stack emission composition. In certain situations, it may be advantageous to add the $Na_2S_2O_3$ before sampling. Consult recent references for additional suggestions. Seal the container, shake to mix, and label; mark the fluid level. Retain alkaline absorbing solution blank and analyze with the samples.

7.6.14 Container No. 5 (silica gel for moisture determination). Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the last impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere strongly to the impinger wall. Because the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

7.6.15 Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.

7.7 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

7.7.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_a = Acetone blank residue concentration, mg/mg.

C_p = Type S pitot tube coefficient (nominally 0.84), dimensionless.

c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I = Percent of isokinetic sampling.

m_a = Mass of residue of acetone after evaporation, mg.

M_n = Total amount of particulate matter collected, mg.

M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack-gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/^oR-lb-mole).

T_m = Absolute average dry-gas meter temperature (see Figure 2), K (^oR).

T_s = Absolute average stack-gas temperature (see Figure 2), K (^oR).

T_{std} = Standard absolute temperature, 293K (528^oR).

V_{lc} = Total volume of liquid collected in the impingers and silica gel, mL.

V_m = Volume of gas sample as measured by dry-gas meter, dscm (dscf).

$V_{m(std)}$ = Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack-gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

V_a = Volume of acetone blank, mL.

V_{aw} = Volume of acetone used in wash; mL.

Y = Dry-gas-meter calibration factor, dimensionless.

H = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

ρ_a = Density of acetone, mg/ml (see label on bottle).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

7.7.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 2).

7.7.3 Dry gas volume. Correct the sample measured by the dry gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]) by using Equation 1:

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar} + \Delta H/13.6}{P_{std}} = K_1 V_m Y \frac{P_{bar} + H/13.6}{T_m} \quad (1)$$

where: K_1 = 0.3858 K/mm Hg for metric units, or
K_1 = 17.64°R/in. Hg for English units.

7.7.4 Volume of water vapor.

$$V_{w(std)} = V_{lc} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{lc} \quad (2)$$

where: K_2 = 0.001333 m^3/mL for metric units, or
K_2 = 0.04707 ft^3/mL for English units.

7.7.5 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad (3)$$

NOTE: In saturated or water-droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 3) and a second from the assumption of saturated conditions. The lower of the two values of B_w shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note to Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ± 1°C (2°F).

7.7.6 Acetone blank concentration. For particulate determination.

$$C_a = \frac{m_a}{V_a \rho_a} \quad (4)$$

7.7.7 Acetone wash blank. For particulate determination.

$$W_a = C_a \, V_{aw} \, \rho_a \quad (5)$$

7.7.8 Total particulate weight. Determine the total particulate catch from the sum of the weights obtained from Container Nos. 1 and 2 less the acetone blank (W_a).

7.7.9 Particulate concentration.

$$c_s = (0.001 \text{ g/mg})(m_n/V_{m(std)}) \quad (6)$$

7.7.10 Isokinetic variation.

7.7.10.1 Calculation from raw data.

$$I = \frac{100 \, T_s[K_3 V_{lc} + (V_m/T_m)(P_{bar} + \Delta H/13.6)]}{60 \theta V_s P_s A_n} \quad (7)$$

where: $K_3 = 0.003454$ mm Hg-m^3/mL-K for metric units, or
$K_3 = 0.002669$ in. Hg-ft^3/mL ^oR for English units.

7.7.10.2 Calculation for intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} V_s \, \theta \, A_n P_s 60(1-B_{ws})} \quad (8)$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \, \theta \, (1-B_{ws})}$$

where: $K_4 = 4.320$ for metric units, or
$K_4 = 0.09450$ for English units.

7.7.11 Acceptable results. If 90% $\leq I \leq$ 110%, the results are acceptable.

7.7.12 Analytical calculation for total µg HCl per sample. Calculate as described below:

$$m_{HCl} = S \times V_s \times 36.46/35.45$$

where:

m_{HCl} = Mass of HCl in sample, µg
S = Analysis of sample, µg Cl^-/mL
V_s = Volume of filtered and diluted sample, mL
36.46 = Molecular weight of HCl, µg/µg-mole
35.45 = Molecular weight of Cl^-, µg/µg-mole

7.7.13 Analytical calculation for total µg Cl_2 per sample. Calculate as described below:

$$m_{Cl2} = S \times V_2$$

where:

V_2 = Volume of filtered and diluted sample, mL
S = Analysis of sample, µg Cl^-/mL
m_{Cl2} = Mass of Cl_2 in sample, µg

7.7.14 Concentration of HCl in the flue gas. Calculate as described below:

$$C = K \times m/V_{m(std)}$$

where:

C = Concentration of HCl or Cl_2, dry basis, mg/dscm,
$K = 10^{-3}$ mg/µg,
m = Mass of HCl or Cl_2 in sample, µg, and
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

8.0 QUALITY CONTROL

8.1 Sampling. See EPA Manual 600/4-77-027b for Method 5 quality control.

8.2 Analysis. At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

8.3 Quality control check sample. Chloride solutions of reliably known concentrations are available for purchase from the National Institute of Standards and Technology (SRM 3182). The QC check sample should be prepared in the appropriate absorbing reagent at a concentration approximately equal to the mid range calibration standard. The quality control check sample should be injected in duplicate immediately after the calibration standards have been injected the first time.

The Cl^- value obtained for the check sample using the final calibration curve should be within 10 percent of the known value for the check sample.

9.0 METHOD PERFORMANCE

9.1 The in-stack limit for HCl for the method is approximately 0.02 mg/dscm of stack gas. The method has a negative bias below 20 ppm HCl (Reference 6).

9.2 It is preferable to include the cyclone in the sampling train to protect the filter from any moisture present. There is research in progress regarding the necessity of the cyclone at low moisture sources and the use of Ascarite II in the drying procedure (Section 7.5.12).

9.3 The lower detection limit of the analytical method is 0.1 ug of Cl^- per mL of sample solution. Samples with concentrations which exceed the linear range of the IC may be diluted.

9.4 The precision and bias for analysis of HCl using this analytical protocol have been measured in combination with the midget impinger HCl/Cl_2 train (Method 0051) for sample collection. The laboratory relative standard deviation is within 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm. respectively. The method does not exhibit any bias for HCl when sampling at Cl_2 concentrations less than 50 ppm.

10.0 REFERENCES

1. U. S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Methods 1-5.

2. U. S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods," Publication No. EPA-600/4-77-027b, August 1977.

3. Shigehara, R. T., Adjustments in the EPA Nomography for Different Pitot Tube Coefficients and Dry Molecular Weights, Stack Sampling News, 2:4-11 (October 1974).

4. Steinsberger, S. C. and J. H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U. S. Environmental Protection Agency, Office of Research and Development, Report No. 600/3/89/064, April, 1989. Available from NTIS.

5. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources," March 18, 1987.

6. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

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8. Johnson, L.D., “Stack Sampling Methods for Halogens and Halogen Acids,” presented at EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Trinagle Park, NC, May 1996.

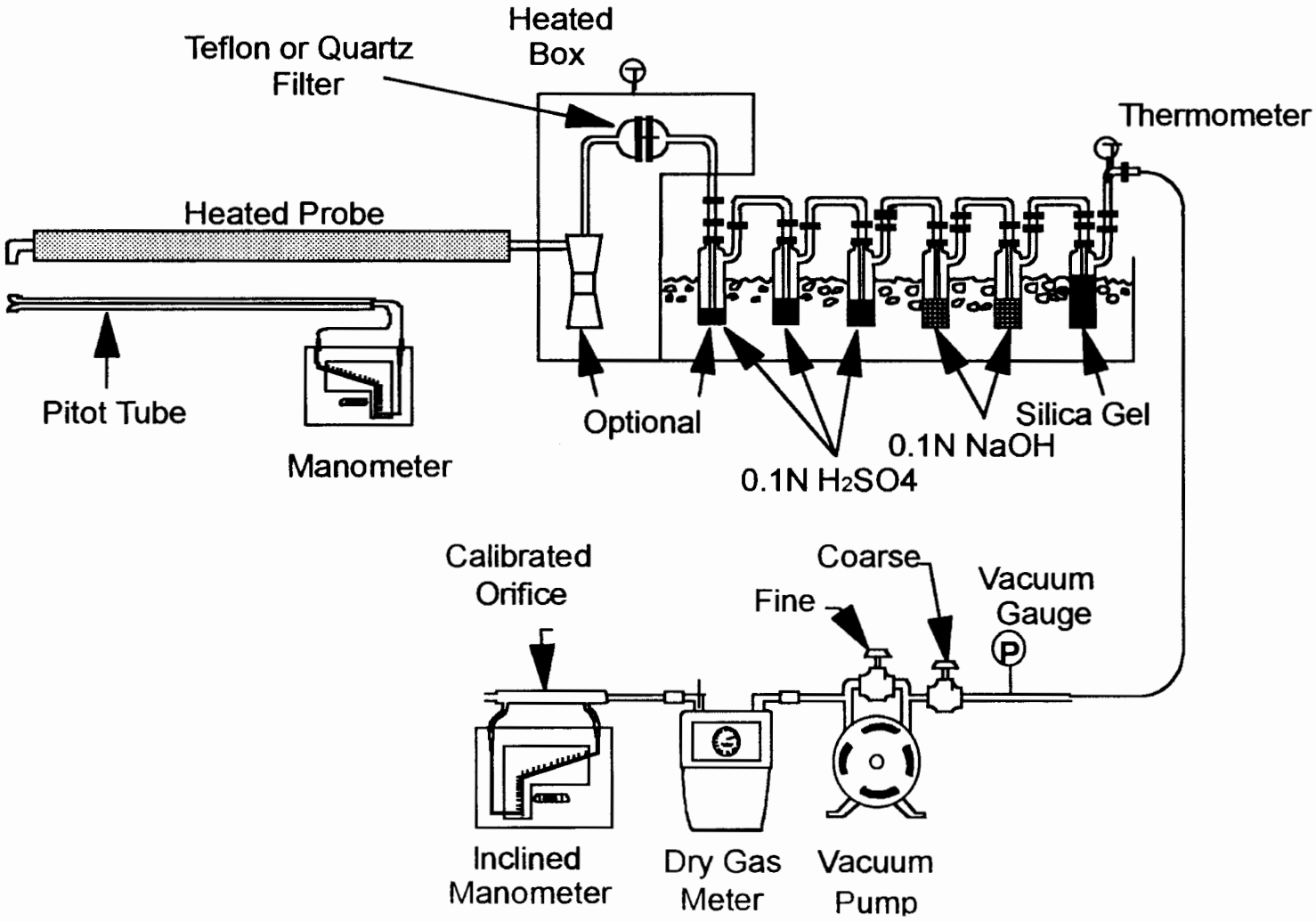


FIGURE 1. ISOKINETIC HCl/Cl_2 SAMPLING TRAIN.

Plant_____
Location_____
Operator_____
Date_____
Run No._____
Sample Box No._____
Meter Box No._____
Meter ??_____
C Factor_____
Pitot Tube Coefficient C_p _____

Schematic of Stack Cross Section

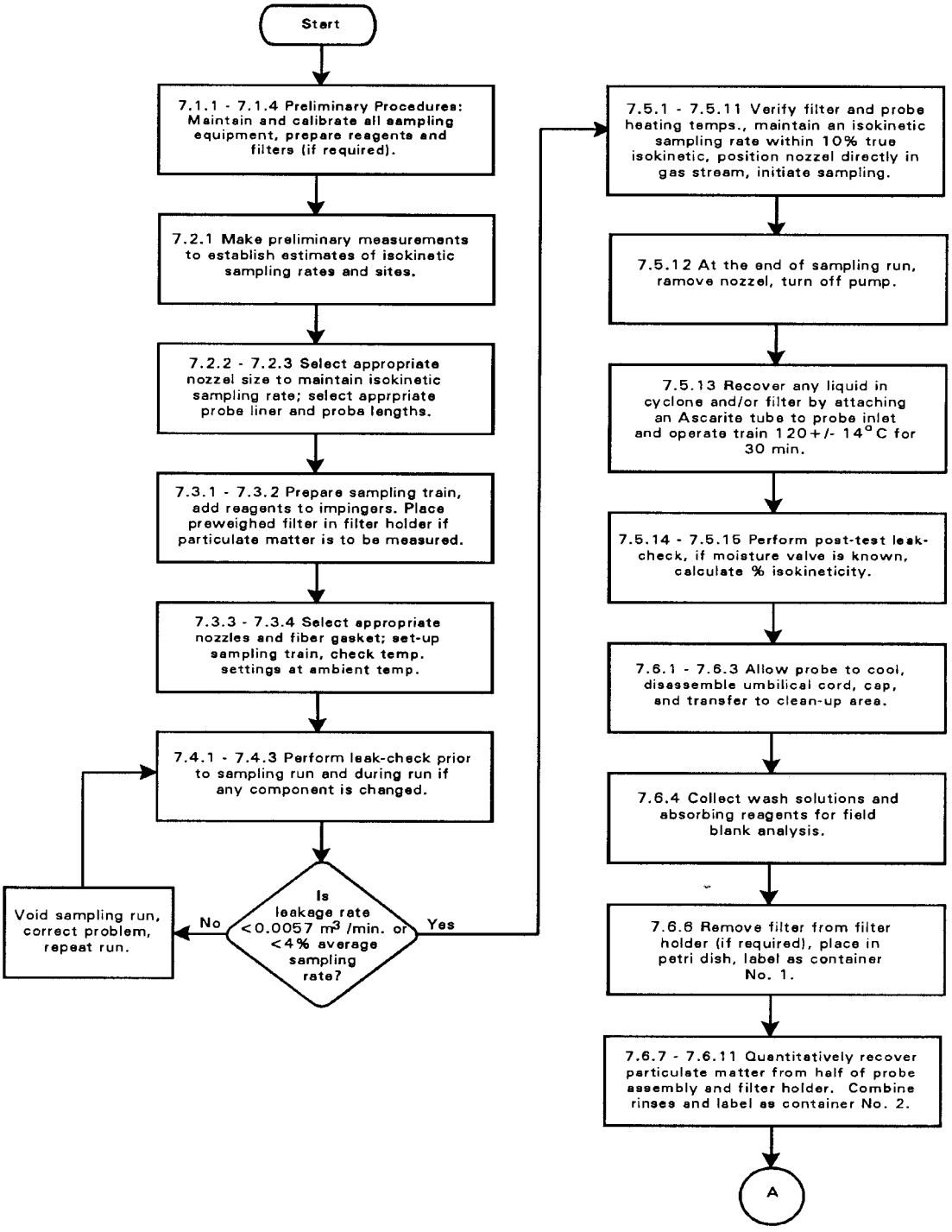
Ambient Temperature_____
Barometric Pressure_____
Assumed Moisture %_____
Probe Length_____
Nozzle Identification No._____
Average Calibrated Nozzle Diameter, cm (in)_____
Probe Heater Setting_____
Leak Rate, m^3/min, (cfm)_____
Probe Liner Material_____
Static Pressure, mm Hg, (in. Hg)_____
Filter No._____

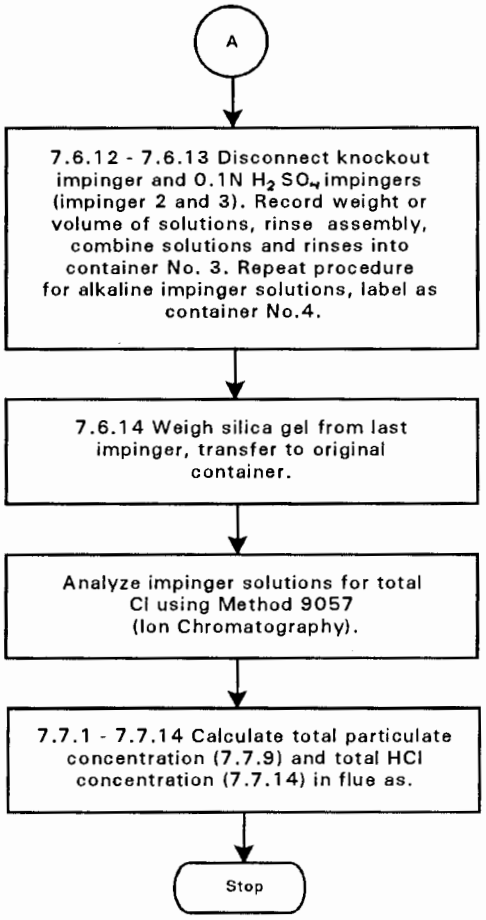
Traverse Point Number	Sampling Time (θ) min	Vacuum mm Hg (in. Hg)	Stack Temp. (T_s) °C (°F)	Velocity Head (P_s) mm (in) H_2O	Pressure Differential Across Orifice Meter mm (in) H_2O	Gas Sample Volume m^3 (ft^3)	Gas Sample Temp. At Dry Gas Meter Inlet °C (°F)	Gas Sample Temp. At Dry Gas Meter Outlet °C (°F)	Filter Holder Temp. °C (°F)		Temp. of Gas Leaving Condenser or Last Impinger
Total							Avg.	Avg.			
Avg.											

FIGURE 2. FIELD DATA FORM.

METHOD 0050

ISOKINETIC HCl/Cl_2 EMISSION SAMPLING TRAIN




A
7.6.12 - 7.6.13 Disconnect knockout impinger and 0.1N H_2SO_4 impingers (impinger 2 and 3). Record weight or volume of solutions, rinse assembly, combine solutions and rinses into container No. 3. Repeat procedure for alkaline impinger solutions, label as container No.4.
7.6.14 Weigh silica gel from last impinger, transfer to original container.
Analyze impinger solutions for total Cl using Method 9057 (Ion Chromatography).
7.7.1 - 7.7.14 Calculate total particulate concentration (7.7.9) and total HCl concentration (7.7.14) in flue as.
Stop

METHOD 0051

MIDGET IMPINGER HCl/Cl_2 EMISSION SAMPLING TRAIN

1.0 SCOPE AND APPLICATION

This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl_2, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators and municipal waste combustors. The collected samples are analyzed using Method 9057. This method is designed to collect HCl/Cl_2 in their gaseous forms. Use of this method is limited to the sampling of relatively dry, particulate-free gas streams. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter (e.g., HCl dissolved in water droplets) must be sampled using an isokinetic HCl/Cl_2 sampling train (see Method 0050). This method has potential for collection of all halogens and halogen acids, but has not been fully evaluated for that use. For analytical determination of additional halides, Method 9056 is used rather than Method 9057.

2.0 SUMMARY OF METHOD

An integrated gas sample is extracted from the stack and passes through a particulate filter, acidified water, and finally through an alkaline solution. The filter serves to remove particulate matter such as chloride salts which could potentially react and form the analyte in the absorbing solutions. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl^-) as follows:

$$HCl + H_2O = H_3O^+ + Cl^-$$

The Cl_2 gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^-, and hypochlorous acid (HClO) as follows:

$$H_2O + Cl_2 = H^+ + Cl^- + HClO$$

The Cl^- ions in the separate solutions are measured by ion chromatography (Method 9057).

Sodium thiosulfate solution is added to the contents of the hydroxide filled impingers, in order to promote the following reaction.

$$S_2O_3^{-2} + 4OCl^- + 2OH^- = 2SO_4^{-2} + 4Cl^- + H_2O$$

Conversion of all the original Cl_2 to the stable Cl^- ion, and appropriate adjustment of the analysis calculations, removes the possibility of partial reduction of OCl^- to Cl^- and the resulting high bias to the results.

3.0 INTERFERENCES

Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl_2) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl_2 gas exhibits

a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl_2 with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4 percent in the HCl measurement.

4.0 APPARATUS AND MATERIALS

4.1 Sampling Train. The sampling train is shown in Figure 1 and component parts are discussed below.

4.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) inside diameter, with a heating system to prevent condensation. When the concentration of alkaline particulate matter in the emissions is high, a 3/8-in. (9-mm) inside diameter Teflon elbow should be attached to the inlet of the probe. A 1-in. (25-mm) length of Teflon tubing with a 3/8-in. (9-mm) inside diameter should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the gas stream, thus reducing the amount of particulate entering the train. When high concentrations of particulate matter are not present, the Teflon elbow is unnecessary, and the probe inlet can be perpendicular to the gas stream. When sampling at locations where gas temperatures are greater than approximately 400°F, such as wet scrubber inlets, glass or quartz elbows must be used. In no case should a glass wool plug be used to remove particulate matter; use of such a filtering device could result in a bias in the data. Instead, a Teflon filter should be used as specified in Section 5.5.

4.1.2 Three-way stopcock. A borosilicate, three-way glass stopcock with a heating system to prevent condensation. The heated stopcock should connect directly to the outlet of the probe and filter assembly and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

4.1.3 Impingers. Five 30-ml midget impingers with leak-free glass connectors. For sampling at high moisture sources or for extended sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

4.1.4 Mae West impinger or drying tube. Mae West design impinger (or drying tube, if a moisture determination is not to be conducted) filled with silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump.

4.1.5 Sample line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

4.1.6 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for the elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

4.1.7 Purge pump, purge line, drying tube, needle valve, and rate meter. Pump capable of purging sample probe at 2 liters/min. with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter, 0 to 5 liters/min.

4.1.8 Metering system. The following items comprise the metering system which is identical to that used for EPA Method 6 (see Reference 5).

4.1.8.1 Valve. Needle valve, to regulate sample gas flow rate.

4.1.8.2 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through train. Install a small surge tank between the pump and the rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

4.1.8.3 Rate meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of selected flow rate of 2 liters/min.

4.1.8.4 Volume meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions encountered during sampling, and equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within 3°C (5.4°F).

4.1.8.5 Vacuum gauge. At least 760 mm Hg (30 in. Hg) gauge to be used for leak check of the sampling train.

4.1.9 Water Bath: To minimize loss of absorbing solution

4.2 Sample Recovery.

4.2.1 Wash bottles. Polyethylene or glass, 500 ml or larger, two.

4.2.2 Storage bottles. Glass, with Teflon-lined lids, 100 ml, to store impinger samples (two per sampling run).

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. All references to water in the method refer to reagent water as defined in Chapter One unless otherwise specified. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values.

5.3 Sulfuric acid (0.05 M), H_2SO_4. Used as the HCl absorbing reagent. To prepare 100 mL, slowly add 0.28 mL of concentrated H_2SO_4 to about 90 mL of water while stirring, and adjust the final volume to 100 mL using additional water. Shake well to mix the solution. It is advisable to

analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values.

5.4 Sodium hydroxide (0.1 M), NaOH. Used as the Cl_2 absorbing reagent. To prepare 100 mL, dissolve 0.40 g of solid NaOH in about 90 mL of water and adjust the final volume to 100 mL using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample value.

5.5 Filter. Teflon mat Pallflex® TX40HI75 or equivalent. Locate in a glass, quartz, or Teflon filter holder with a Teflon filter support in a filter box heated to 250°F.

5.6 Sodium thiosulfate (0.5 M), $Na_2S_2O_3$. Used as the reducing agent added to the sodium hydroxide filled impingers to promote the reaction given in Section 2.0. Buy premixed reagent grade, as free of chloride as possible.

5.7 Silica gel. Indicating type, 6- to 16-mesh. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection is described in this method. The analytical procedures are described in Method 9057.

6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

7.0 PROCEDURE

7.1 Calibration. Section 3.5.2 of EPA's Quality Assurance Handbook Volume III (Reference 4) may be used as a guide for these operations.

7.1.1 Dry Gas Metering System.

7.1.1.1 Initial calibration. Before its initial use in the field, first leak check the metering system (sample line, drying tube, if used, vacuum gauge, needle valve, pump, rate meter, and dry gas meter) as follows: plug the inlet end of the sampling line, pull a vacuum of 250 mm (10 in.) Hg, plug off the outlet of the dry gas meter, and turn off the pump. The vacuum should remain stable for 30 seconds. Carefully release the vacuum from the system by slowly removing the plug from the sample line inlet. Remove the sampling line (and drying tube, if applicable), and connect the dry gas metering system to a appropriately sized wet test meter (e.g., 1 liter per revolution). Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, with both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 percent from the average, the

metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

7.1.1.2 Post-test calibration check. After each field test series, conduct a calibration check as in Section 7.1.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three or more revolutions of the dry gas meter may be used, (c) only two independent runs need to be made. If the calibration factor does no deviate by more than 5 percent from the initial calibration factor (determined in Section 7.1.1.1), the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as Section 7.1.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

7.1.2 Thermometer(s). Prior to each field test, calibrate against mercury-in-glass thermometers at ambient temperature. If the thermometer being calibrated reads within 2°C (2.6°F) of the mercury-in-glass thermometer, it is acceptable. If not, adjust the thermometer or use an appropriate correction factor.

7.1.3 Rate meter. The rate meter should be cleaned and maintained according to the manufacturer's instructions.

7.1.4 Barometer. Prior to each field test, calibrate against a mercury barometer. The field barometer should agree within 0.1 in. Hg with the mercury barometer. If it does not, the field barometer should be adjusted.

7.2 Sampling.

7.2.1 Preparation of collection train. Prepare the sampling train as follows: The first or knockout impinger should have a shortened stem and be left empty to condense moisture in the gas stream. The next two midget impingers should each be filled with 15 mL of 0.05 M H_2SO_4. The fourth and fifth impingers should each be filled with 15 mL of 0.1 M NaOH. It is essential that the NaOH filled impingers be maintained strongly basic throughout the sampling run. In highly acid stack environments, this may require measures such as stronger base, more volume of basic solution, or changeout of impinger liquid during the run. When in doubt the pH of the solution should be monitored frequently or continuously. Place a fresh charge of silica gel, or equivalent, in the Mae West impinger (or the drying tube). Connect the impingers in series with the knockout impinger first, followed by the two impingers containing the acidified reagent and two impingers containing the alkaline reagent, and the Mae West impinger containing the silica gel. If the moisture will be determined, weigh the impinger assembly to the nearest $\pm$ 0.5 g and record the weight.

7.2.2 Leak check procedures. Leak check the probe and three-way stopcock prior to inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Place the probe in the stack at the sampling location, and adjust the filter heating system to 121°C (250°F) and the probe and stopcock heating systems to a temperature sufficient to

prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to the last impinger and the needle valve. Upon completion of a sampling run, remove the probe from the stack and leak check as described above. If a leak has occurred, the sampling run must be voided. Alternatively, the portion of the train behind the probe may be leak checked between multiple runs at the same site as follows: Close the stopcock to the first impinger, and turn on the sample pump. Pull a vacuum of at least 250 mm Hg (10 in. Hg), turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Release the vacuum on the impinger train by turning the stopcock to the vent position to permit ambient air to enter. If this procedure is used, the full train leak check described above must be conducted following the final run and all preceding sampling runs voided if a leak has occurred.

7.2.3 Purge procedures. Immediately prior to sampling, connect the purge line to the stopcock and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes prior to sampling.

7.2.4 Sample collection. Turn on sample pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C). Adjust the sampling rate to 2 liters/min. as indicated by the rate meter, and maintain this rate within 10 percent during the entire sampling run. Take readings of the dry gas meter, the dry gas meter temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. However, if the expected condensate catch for this sampling run duration will exceed the capacity of the sampling train, (1) a larger knockout impinger may be used or (2) two sequential half-hour runs may be conducted. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak check as described in Section 7.2.2.

7.3 Sample recovery. Following sampling, disconnect the impinger train from the remaining sampling equipment at the inlet to the knockout impinger and the outlet to the last impinger. If performing a moisture determination, wipe off any moisture on the outside of the train; weigh the train to the nearest 0.5 g and record the weight. Then disconnect the impingers from each other. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two 0.05 M H_2SO_4 impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle. The contents of the impingers and connecting glassware from the second set of impingers (containing the 0.1 M NaOH) should be recovered in a similar manner if a Cl_2 analysis is desired. Add 2 mL or more of 0.5 M $Na_2S_2O_3$. to the sodium hydroxide (Cl_2) samples. It is necessary to add sufficient $Na_2S_2O_3$ to reduce the OCl^-, but too much thiosulfate may interfere with the ion chromatography analysis. The amount needed will vary with stack emission composition. In certain situations, it may be advantageous to add the $Na_2S_2O_3$ before sampling. Consult recent references for additional suggestions. The sample bottle should be sealed, shaken to mix, and labeled; the fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Save portions of the 0.05 M H_2SO_4 and 0.1 M NaOH used as impinger reagents as reagent blanks. Take 50 ml of each and place in separate leak-free storage bottles. Label and mark the fluid levels as previously described.

7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

7.4.1 Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Average dry gas meter absolute temperature, K (°R).

T_{std} = Standard absolute temperature, 293K (528°R).

V_{lc} = Total volume of liquid collected in impingers and silica gel, mL (equivalent to the difference in weight of the impinger train before and after sampling, 1 mg = 1 mL).

V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

Y = Dry gas meter calibration factor.

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

7.4.2 Sample volume, dry basis, corrected to standard conditions. Calculate as described below:

$$V_{m(std)} = V_m Y \frac{T_{std}}{T^m} \frac{P_{bar}}{P_{std}} = K_1 Y \frac{V_m P_{bar}}{T_m} \quad (1)$$

where:

K_1 = 0.3858K/mm Hg for metric units.
= 17.64°R/in. Hg for English units.

7.4.3 Volume of water vapor.

$$V_{w(std)} = V_{lc} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{lc} \quad (2)$$

where:

K_2 = 0.0013333 m^3/mL for metric units.
= 0.04707 ft^3/mL for English units.

7.4.4 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad (3)$$

7.4.5 Analytical calculation of total ug HCl per sample. Calculate as described below:

$$m_{HCl} = S \times V_s \times 36.46/35.45$$

where:

m_{HCl} = Mass of HCl in sample, µg
S = Analysis of sample, µg Cl^-/mL
V_s = Volume of filtered and diluted sample, mL
36.46 = Molecular weight of HCl, µg/µg-mole
35.45 = Molecular weight of Cl^-, µg/µg-mole

7.4.6 Analytical calculation of total µg Cl_2 per sample. Calculate as described below:

$$m_{Cl2} = S \times V_2$$

where:

V_2 = Volume of filtered and diluted sample, mL
S = Analysis of sample, µg Cl^-/mL
m_{Cl2} = Mass of Cl_2 in sample, µg

7.4.7 Concentration of HCl in the flue gas. Calculate as described below:

$C = K \times m/V_{m(std)}$

where: C = Concentration of HCl or Cl_2, dry basis, mg/dscm,
K = 10^{-3} mg/µg,
m = Mass of HCl or Cl_2 in sample, µg, and
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

8.0 QUALITY CONTROL

8.1 At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

8.2 Quality control check sample. Chloride solutions of reliably known concentrations are available for purchase from the National Bureau of Standards (SRM 3182). The QC check sample should be prepared in the appropriate absorbing reagent at a concentration approximately equal to the mid range calibration standard. The quality control check sample should be injected in duplicate immediately after the calibration standards have been injected the first time. The Cl^- value obtained for the check sample using the final calibration curve should be within 10 percent of the known value for the check sample.

9.0 METHOD PERFORMANCE

9.1 The in-stack limit for HCl for the method is approximately 0.08 mg/dscm of stack gas for a 1-hour sample.

9.2 The precision and bias for measurement of HCl using this sampling protocol combined with the analytical protocol, Method 9057, have been determined. The laboratory relative standard deviation is within 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at Cl_2 concentrations less than 50 ppm.

10.0 REFERENCES

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5. U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Method 6.

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7. Johnson, L.D.,"Stack Sampling Methods for Halogens and Halogen Acids," presented at EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996.

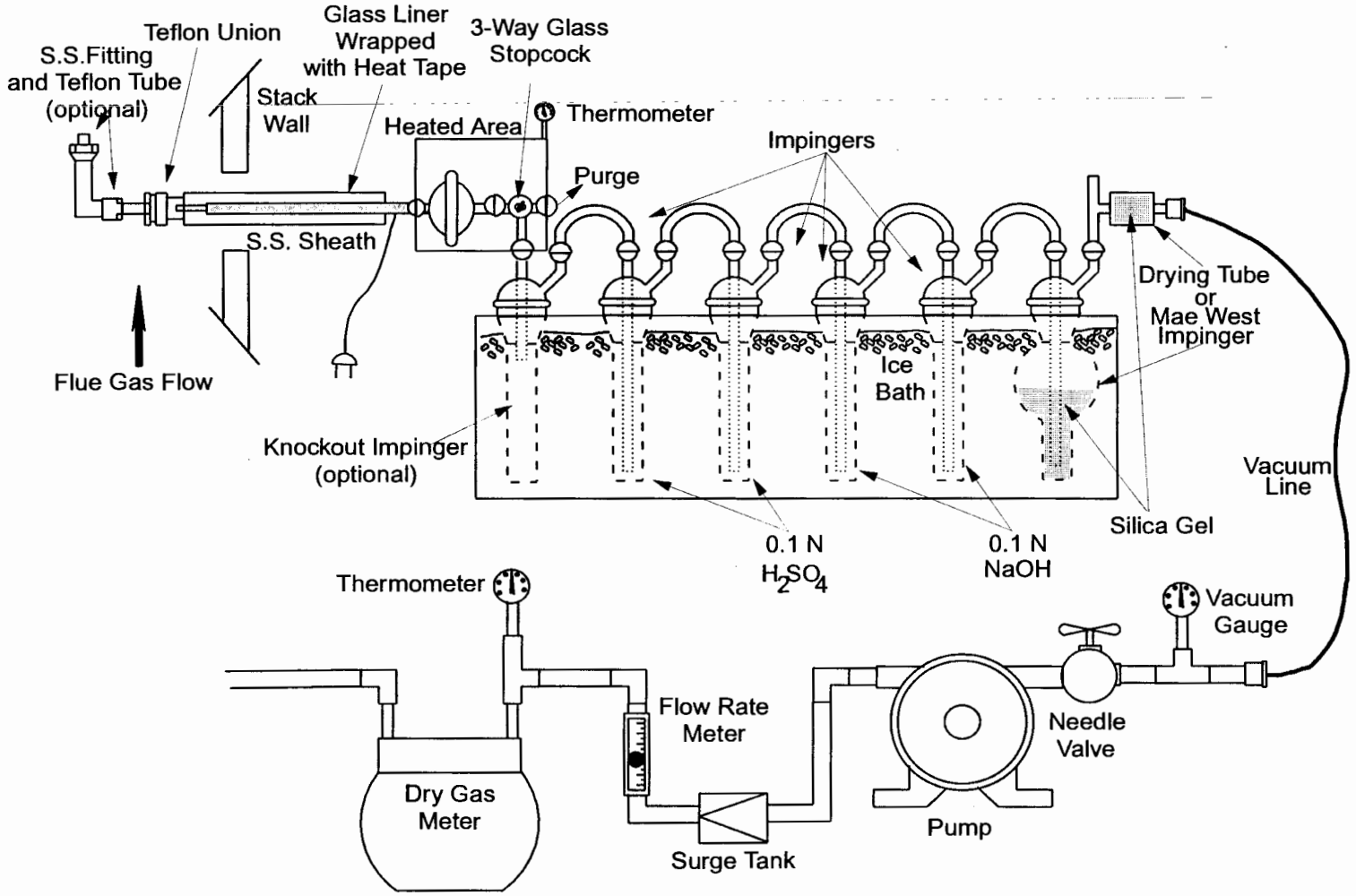
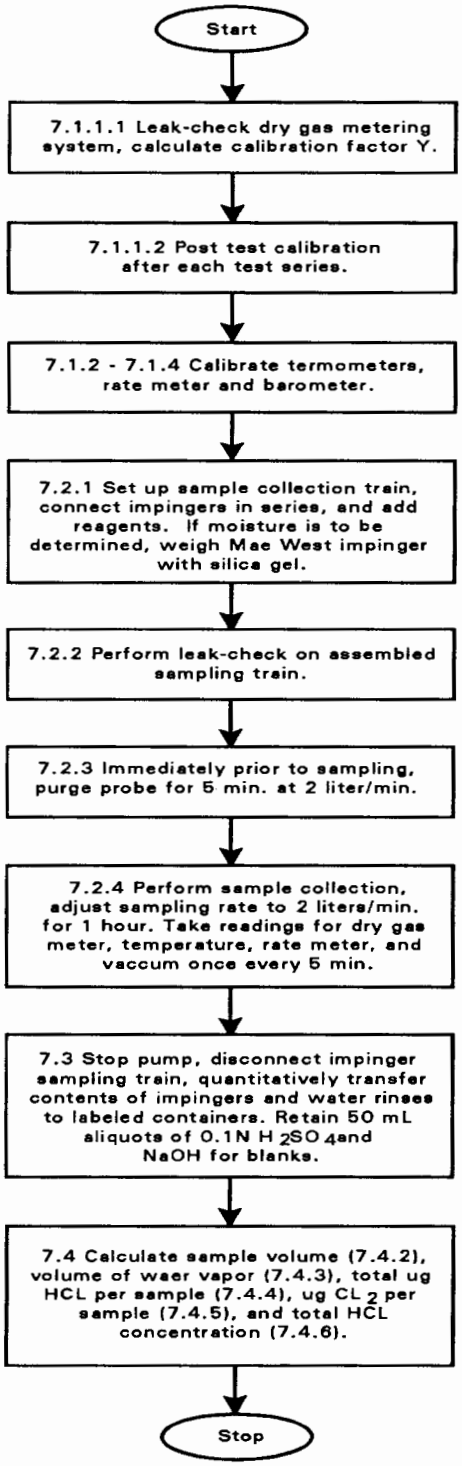


FIGURE 1. METHOD 0051 SAMPLING TRAIN

METHOD 0051

MIDGET IMPINGER HCl/Cl_2 EMISSION SAMPLING TRAIN



METHOD 0060

DETERMINATION OF METALS IN STACK EMISSIONS

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of metals in stack emissions from hazardous waste incinerators and similar combustion processes. Using the detection limits shown, the following parameters can be determined by this method:

TABLE 1. ESTIMATED IDLS FOR METALS DETERMINED BY METHOD 0060

Analyte	ICP-AES[a] µg/L	Flame AA[b] µg/L	GFAA[c] µg/L	CVAA[d] µg/L
Antimony (Sb)	40[e]	200[e]	3[e]	
Arsenic (As)	60	2[f]	1	
Barium (Ba)	2	100		
Beryllium (Be)	0.3	5	0.2	
Cadmium (Cd)	4	5	0.1	
Total chromium (Cr)	7	50	1	
Cobalt (Co)	7	50	1	
Copper (Cu)	6	20		
Lead (Pb)	50	100	1	
Manganese (Mn)	2	10		
Mercury (Hg)				0.2
Nickel (Ni)	20	40		
Phosphorus (P)	60			
Selenium (Se)	80	2[f]	2	
Silver (Ag)	7	10		
Thallium (Tl)	40	100	1	
Zinc (Zn)	2	5		

a Estimated IDLs by ICP-AES, Method 6010.
b Estimated IDLs by direct aspiration Flame AA, Method 7000.
c Estimated IDLs by Graphite Furnace AA, Method 7000.
d Estimated IDL by Cold Vapor AA, Method 7470.
e Detection limit for Sb may be higher depending on digestion used.
f Estimated IDLs for As and Se by Hydride AA, Method 7000.

1.2 This method may also be used for the determination of particulate emissions following the additional procedures described in Section 7.1.5.2.

1.3 For the analyses described in this methodology and for similar analyses, the response for Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) is linear over several

orders of magnitude. Samples containing metal concentrations in the micrograms per liter (µg/L) to milligrams per liter (mg/L) range in the final analytical solution can be analyzed using this technique. Samples containing greater than approximately 50 mg/L of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 mg/L of cadmium should be diluted to that level before analysis.

1.4 The actual method detection limits are sample dependent and may vary as the sample matrix affects the limits. Method detection limits for antimony can also be dependent on the digestion method used and may be considerably higher than the estimated detection limits. Method detection limits for all analytes may differ from the estimated detection limits when hydrofluoric acid digestion is used. For more information on MDLs, refer to Chapter One.

1.5 The complexity of this methodology is such that to obtain reliable results, the testers (including analysts) should be experienced and as knowledgeable as required in source sampling, in handling and preparing (including mixing) reagents as discussed, and in using adequate safety procedures and protective equipment. The experience and knowledge should assure adequacy as described above in all of the source emission determination activities including planning of the desired detection limits.

2.0 SUMMARY

2.1 The stack sample is withdrawn isokinetically from the source. Particulate emissions are collected in the probe and on a heated filter and gaseous emissions are collected in a series of chilled impingers as shown in Figure 1 and described in Section 4.1.6. Two impingers are empty, two impingers contain an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide, two other impingers contain acidic potassium permanganate solution, and the last impinger contains a desiccant.

2.2 Sampling train components are recovered and digested in separate front-half and back-half fractions. Materials collected in the sampling train are acid digested to dissolve inorganics and to remove organic constituents that may create analytical interferences. Acid digestion is performed by using either digestion techniques of this manual, or the Method 29 (Ref. 3) procedures.

2.3 The nitric acid and hydrogen peroxide impinger solution, the hydrochloric acid rinse solution, the acidic potassium permanganate impinger solution, and the probe rinse and digested filter solutions are analyzed for mercury by Cold Vapor Atomic Absorption Spectrometry (CVAA). All of the sampling train catches, except for the permanganate solution, hydrochloric acid rinse solutions, and reagent water used to recover Hg, may be analyzed for target metals as presented in Table 1 by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) or Flame Atomic Absorption Spectrometry (FLAA). Similarly, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, As, Tl and Zn. If antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, selenium, and thallium require greater analytical sensitivity than can be obtained by ICP-AES, then Graphite Furnace Atomic Absorption Spectrometry (GFAA) is used for the analysis. Additionally, if desired, the tester may use FLAA for analyses of all metals if the resulting in-stack method detection limits meet the goal of the testing program.

2.4 For convenience, aliquots of each digested sample Fraction 1A, as described in Section 7.2.3.2, plus Fraction 2A, as described in Section 7.2.4, can be combined for a single

analytical determination, proportionally with respect to the original Fractions 1A and 2A. Fraction 1A is normally diluted to 300 mL following digestion prior to analysis and the concentrated Fraction 2A is normally diluted to 150 mL following digestion and prior to analysis.

2.5 The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals and/or other quality assurance measures as described in Section 8.0 of this method including actual sample matrix effects checks.

3.0 INTERFERENCES

3.1 Refer to the appropriate determinative method for instructions on minimization of interferences.

4.0 APPARATUS AND MATERIALS

4.1 Sampling train - A schematic of the sampling train is shown in Figure 1. It is similar to the Method 5 (Ref. 3) train. The sampling train consists of the following components.

4.1.1 Probe nozzle (probe tip) and borosilicate or quartz glass probe liner - Same as Method 5, except that glass nozzles are required unless an alternate probe tip prevents the possibility of contamination or interference of the sample with its materials of construction. If a probe tip other than glass is used, no correction of the stack sample test results can be made because of the effect on the results by the probe tip.

4.1.2 Pitot tube and differential pressure gauge - Same as Method 2 (Ref. 3).

4.1.3 Filters - Quartz fiber or glass fiber filters without organic binders shall be used. The filters shall contain less than 1.3 µg/in.^{2} of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test should be conducted in accordance with ASTM Standard Method D2986-71 (Reference 4). For particulate determination in sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3, as described Method 5. Quartz fiber filters that meet these requirements are recommended.

4.1.4 Filter holder - Glass, same as Method 5, except that a Teflon filter support or other non-metallic, non-contaminating support must be used to replace the glass frit.

4.1.5 Filter heating system - Same as Method 5.

4.1.6 Condenser

4.1.6.1 The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The condensing system should consist of three to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Teflon impingers of substantially the same shape, size and function

compared to the glass impingers and connected with leak-free non-contaminating fittings may be used: - additionally, the distance from the bottom of the gas conduit stem of the Teflon impinger assembly to the bottom of the portion of the impinger assembly which holds the aqueous acidic solutions must meet the same distance requirements as the glass impingers. The first impinger is optional and is recommended as a moisture knockout trap for use during test conditions which require such a trap. The first impinger shall be empty. The second and third impingers shall contain known quantities of a nitric acid/hydrogen peroxide solution (Section 5.8). The fourth shall be empty. The fifth and sixth impingers shall contain a known quantity of acidic potassium permanganate solution (Section 5.12), and the last impinger shall contain a known quantity of silica gel or equivalent desiccant. A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger.

4.1.6.2 The first impinger shall be appropriately sized for a potentially large moisture catch and constructed generally as described for the first impinger in Method 5. The second impinger (or the first HNO_3/H_2O_2 impinger) shall also be as described for the first impinger in Method 5. The third impinger (or, in any case, the impinger used as the second HNO_3/H_2O_2 impinger) shall be the same as the Greenburg-Smith impinger with the standard tip described as the second impinger in Method 5. All other impingers used in the metals train are the same as the first HNO_3/H_2O_2 impinger.

4.1.6.3 Based on the specific source sampling conditions, the use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 mL. When the moisture knockout impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not to be performed, the potassium permanganate impingers and the empty impinger preceding them are removed.

4.1.7 Metering system, barometer, and gas density determination equipment - Same as Method 5.

4.1.8 Teflon tape - For capping openings and sealing connections, if necessary, on the sampling train.

4.2 Sample recovery. Same as Method 5, with the following exceptions and additions:

4.2.1 Non-metallic probe-liner and probe-nozzle brushes or swabs - For quantitative recovery of materials collected in the front half of the sampling train. Description of acceptable all-Teflon component brushes or swabs to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

4.2.2 Sample storage containers - Glass bottles, 1000 mL and 500 mL, with Teflon-lined caps which are non-reactive to oxidizing solutions, shall be used for samples and blanks containing $KMnO_4$. Polyethylene bottles may be used for other sample types.

4.2.3 Polypropylene tweezers and/or plastic gloves - For recovery of the filter from the sampling train filter holder.

4.3 Sample preparation and analysis equipment.

4.3.1 Refer to the appropriate preparation and analytical techniques for the proper apparatus and materials. Refer to Section 7.2 for a description of preparation techniques.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise use the best available grade.

5.2 Reagent Water. Refer to Chapter One for a definition of reagent water. Analyze the water for all target metals prior to field use. All target metals should be less than the MDL.

5.3 Nitric acid, concentrated - Baker Instra-analyzed or equivalent.

5.4 Nitric acid (0.1 M) - Add, with stirring, 6.3 mL of concentrated HNO_3 to a flask containing approximately 900 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 µg/L of each target metal.

5.5 Nitric acid, 10 percent (V/V). Add, with stirring, 500 mL of concentrated HNO_3 to a flask containing approximately 4000 mL of water. Dilute to 5000 mL with water. Mix well. Reagent shall contain less than 2 µg/L of each target metal.

5.6 Nitric acid, 5 percent (V/V). Add, with stirring, 50 mL of concentrated HNO_3 to 800 mL of water. Dilute to 1000 mL with water. Reagent shall contain less than 2 µg/L of each target metal.

5.7 Nitric acid, 50 percent (V/V). Add, with stirring, 125 mL of concentrated HNO_3 to a flask containing approximately 100 mL of water. Dilute to 250 mL with water. Mix well. Reagent shall contain less than 2 µg/L of each target metal.

5.8 Nitric acid (HNO_3)/hydrogen peroxide (H_2O_2) absorbing solution, 5 percent HNO_3/10 percent H_2O_2. Add carefully, with stirring, 50 mL of concentrated HNO_3 to a 1000-mL volumetric flask containing 500 mL of water. Carefully add 333 mL of 30% H_2O_2 to the flask. Dilute to volume with water. The reagent shall contain less than 2 µg/L of each target metal.

5.9 Hydrochloric acid (8M), HCl - Carefully add with stirring 690 mL of concentrated HCl to a flask containing 250 mL of water. Dilute to 1000 mL with water. Mix well. The reagent shall contain less than 2 µg/L of Hg.

5.10 Hydrogen peroxide, 30 percent (V/V).

5.11 Potassium permanganate, 5 percent (W/V).

5.12 Acidic potassium permanganate ($KMnO_4$) absorbing solution, 4 percent $KMnO_4$ (W/V), 10 percent H_2SO_4 (V/V) - Prepare fresh daily. Carefully mix 100 mL of concentrated H_2SO_4 into 800 mL of water. Add water, with stirring, to make a volume of 1000 mL. This solution is 10% H_2SO_4

(V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into sufficient 10% H_2SO_4 to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 µg/L of Hg.

CAUTION: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles should not be fully filled and should be vented both to relieve excess pressure and prevent explosion due to pressure buildup. Venting is highly recommended, but should not allow contamination of the solution; a No. 70-72 hole drilled in the container cap and Teflon liner is suggested.

5.13 Sulfuric acid, concentrated.

5.14 Silica gel and crushed ice - Same as Method 5.

5.15 Hydrofluoric acid, concentrated.

5.16 Refer to the appropriate preparation and analytical technique for reagent and standard preparation procedures.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sampling. The complexity of this method is such that, to obtain reliable results, testers should be trained and experienced with the test procedures.

6.1.1 Pretest preparation. Follow the same general procedure given in Method 5, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with reagent water. All glassware should then be soaked in a 10% (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with reagent water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled, prior to sampling.

6.1.2 Sampling train calibration. Maintain a laboratory log of all calibrations. Calibrate the sampling train components according to the appropriate sections of Method 5: probe nozzle; pitot tube; metering system; probe heater; temperature gauges; leak-check of the metering system; and barometer.

6.1.3 Preliminary determinations. Same as Method 5.

6.1.4 Preparation of Sampling Train.

6.1.4.1 Follow the same general procedures given in Method 5, except place 100 mL of the nitric acid/hydrogen peroxide solution (Section 5.8) in each of the two HNO_3/H_2O_2 impingers (normally the second and third impingers) as shown in Figure 1. Place 100 mL of the acidic potassium permanganate absorbing solution (Section

5.12) in each of the two permanganate impingers. Transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

6.1.4.2 Several options are available to the tester based on the sampling conditions. The empty first impinger is not needed if the moisture to be collected in the impingers is calculated or determined to be less than 100 mL.

6.1.4.3 Retain for reagent blanks, volumes of the nitric acid/hydrogen peroxide solution and 100 mL of the acidic potassium permanganate solution. These reagent blanks should be labeled and analyzed as described in Section 7. Set up the sampling train as shown in Figure 1. If necessary to ensure leak-free sampling train connections, Teflon tape or other non-contaminating material should be used instead of silicone grease to prevent contamination.

CAUTION: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for manganese. Prevent hydrogen peroxide from mixing with the acidic potassium permanganate.

6.1.4.4 Alternatively, mercury emissions can be measured in a separate train which measures only mercury emissions by using Method 101A (use only the version of Method 101A which incorporates the changes promulgated on April 25, 1996, in 61 FR 18278 through 18280, or later).

6.1.5 Leak-check procedures. Follow the leak-check procedures given in Method 5: pretest leak-check, leak-checks during the sample run, and post-test leak-checks.

6.1.6 Sampling train operation. Follow the procedures given in Method 5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5. When sampling for Hg, use a procedure analogous to that described in Section 7.1.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger.

6.1.7 Calculation of percent isokinetic. Same as Method 5.

7.0 PROCEDURE

7.1 Sample recovery. Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period.

7.1.1 The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a vacuum to form in the filter holder, thus causing the undesired result of drawing liquid from the impingers into the filter.

7.1.2 Before moving the sampling train to the cleanup site, remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

7.1.3 Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

7.1.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions.

7.1.5 The sample is recovered and treated as follows (see schematic in Figure 2). Assure that all items necessary for recovery of the sample do not contaminate it.

7.1.5.1 Container No. 1 (filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean disposable surgical gloves rinsed with water should be used to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

NOTE: Follow the procedure in Section 7.1.5.2 only if determination of particulate emissions are desired in addition to metals emissions. If only metals emissions are to be determined, skip Section 7.1.5.2 and go to Section 7.1.5.3.

7.1.5.2 Container No. 2 (acetone rinse).

7.1.5.2.1 Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting (fittings made of plastic such as Teflon, polypropylene, etc. are recommended to prevent contamination by metal fittings, further, if desired a single glass piece may be used, but it is not a requirement of this methodology), probe liner, and front half of the filter holder by washing these components with 100 mL of acetone and placing the wash in a glass container. The use of exactly 100 mL is necessary for the subsequent blank correction procedures. Reagent water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Adminstrator; in these cases, save a water blank and follow the Administrators directions on analysis. In these cases, save a water blank. Perform the acetone rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, after which

make a final rinse of the inside surface with acetone. Brush and rinse the sample exposed inside of the Swagelok fitting with acetone in a similar way until no visible particles remain.

7.1.5.2.2 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a nonmetallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe. Rinse and brush three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

7.1.5.2.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

7.1.5.2.4 Clean the inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

7.1.5.3 Container No. 3 (probe rinse). Keep the probe assembly clean and free from contamination as described in Section 7.1.5.2 during the 0.1M nitric acid rinse described below. Rinse the probe liner, probe nozzle, and filter, and front half of the filter holder thoroughly with 100 mL of 0.1 M nitric acid and place the wash into a sample storage container.

NOTE: The use of exactly 100 mL is necessary for the subsequent blank correction procedures. Perform the rinses as applicable and generally as described in Method 12, Section 5.2.2. Record the volume of the combined rinse. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water followed by acetone and discard these rinses.

7.1.5.4 Container No. 4 (Impingers 1 through 3, HNO_3/H_2O_2 impingers and moisture knockout impinger, when used, contents and rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from Impingers 1, 2, and 3 in more than one container. Measure the liquid in the first three impingers volumetrically to within 0.5 mL using a graduated cylinder or weigh quantitatively to 0.5 g using **calibrated** scales. Record the volume of liquid present. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 mL of 0.1 M nitric acid using the procedure as applicable and generally as described in Method 12, Section 5.2.4.

NOTE: The use of exactly 100 mL of 0.1 M nitric acid rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Mark the height of the fluid level on outside of container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

7.1.5.5 Containers No. 5A (0.1M HNO_3), 5B ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8M HCl rinse and dilution). If mercury is not being measured in this train, then Impingers 4, 5, and 6, as shown in Figure 1, are not necessary and may be eliminated.

7.1.5.5.1 Pour all the liquid, if any, from the impinger which was empty at the start of the run (normally Impinger 4) and which precedes the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 mL. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Sample Container No. 5A. Rinse the impinger (No. 4) with 100 mL of 0.1M HNO_3 and place this into Container No. 5A. Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 mL. This information is required to calculate the moisture content of the sampled flue gas. Place this $KMnO_4$ absorbing solution stack sample from the two permanganate impingers into Container No. 5B. Using 100 mL total of the fresh acidified potassium permanganate solution, rinse the permanganate impinger and connecting glass pieces a minimum of three times. Place the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers into Container No. 5B. Using 100 mL total of water, rinse the permanganate impingers and connecting glass pieces a minimum of three times, and place the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated material, if any, from the two impingers into Container No. 5B. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and properly prepare the bottle and clearly label the contents.

NOTE: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle. These bottles shall not be filled full and shall be vented to relieve excess pressure. Venting is required. A No. 70-72 hole drilled in the container cap and Teflon liner is suggested.

7.1.5.5.2 If no visible deposits remain after the above described water rinse, do not rinse with HCl. The previous rinses are designed to remove all of the

permanganate residues, but if any remain, perform the HCl cleanup in a well ventilated area or vent hood as necessary to prevent exposure to any chlorine gases which may be released by the following HCl cleanup procedure. If deposits do remain on the glassware after this water rinse, wash the impinger surfaces with 25 mL of 8M HCl, and place the wash in a separate sample container labeled Container No. 5C that contains 200 mL of water. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 mL of 8M HCl for rinsing both permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 mL of 8M HCl rinse carefully with stirring into Container No. 5C. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport.

7.1.5.6 Container No. 6 (silica gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5g.

7.1.5.7 Container No. 7 (acetone blank). If particulate emissions are to be determined, at least once during each field test, place 100-mL portion of the acetone used in the sample recovery process into a labeled container for use in the front-half field reagent blank. Seal the container.

7.1.5.8 Container No. 8A (0.1 M nitric acid blank). At least once during each field test, place 300 mL of the 0.1 M nitric acid solution used in the sample recovery process into a labeled container for use in the sample recovery process into a labeled container for use in the front-half and back-half field reagent blanks. Seal the container.

7.1.5.9 Container No. 8B (water blank). At least once during each field test, place 100 mL of the water used in the sample recovery process into a labeled Container No. 8B. Seal the container.

7.1.5.10 Container No. 9 (5 percent nitric acid/10 percent hydrogen peroxide blank). At least once during each field test, place 200 mL of the 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use in the back-half field reagent blank. Seal the container.

7.1.5.11 Container No. 10 (acidified potassium permanganate blank). At least once during each field test, place 100 mL of the acidified potassium permanganate solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back-half field reagent blank for mercury analysis. Prepare the container as described in Section 7.2.5.5.1 note.

7.1.5.12 Container No. 11 (8M HCl blank). At least once during each field test, place 200 mL of water into a sample container. Then pour 25 mL of 8M HCl carefully with stirring into the 200 mL of water in the container. Mix well and seal the container.

7.1.5.13 Container No. 12 (filter blank). Once during each field test, place an unused filter from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. This will be used in the front-half field reagent blank.

7.2 Sample preparation. Note the level of the liquid in each of the containers and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred either void the sample or use approved methods to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 3. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples. Acid digestion is performed by using either prescribed digestion techniques of this manual, or the Method 29 procedures.

7.2.1 Container No. 1 (filter). If particulate emissions are being determined, then desiccate the filter and filter catch without added heat and weigh to a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual fluorocarbon based microwave pressure relief vessels or Parr® Bombs. Add 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample according to Method 3051. For conventional heating, heat the Parr® Bombs in an oven at 140°C (285°F) for 6 hours following the manufacturer's recommendations for Bomb loading, assembly and disassembly, cleaning, and handling. Cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 7.2.3.

NOTE: Hydrofluoric acid (HF) has been identified as an exceptional health and contact hazard. Burns and other symptoms can be severe and may not appear immediately. The analyst should perform all operations with HF under appropriate laboratory conditions (i.e., in a fume hood suitable for HF work), should be fully informed regarding the appropriate safety data (e.g., all hazard warnings, storage and handling requirements, spill cleanup procedures, and emergency treatments for exposure), and should wear the appropriate laboratory protective equipment (e.g., goggles, face shield, lab coat, rubber apron, long rubber gloves) when preparing and handling digestates and other solutions containing HF.

7.2.2 Container No. 2 (acetone rinse). Measure the liquid in this container either volumetrically to ±1 mL or gravimetrically to ±0.5 g. Transfer the contents to an acid-cleaned tared 250-mL beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 mL concentrated nitric acid and carefully, with stirring, combine the resultant sample including all liquid and any particulate matter with Container No. 3 prior to beginning the Section 7.2.3.

7.2.3 Container No. 3 (probe rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified by careful addition, with stirring, with concentrated nitric acid to pH 2. The sample should be rinsed into a beaker with water and

the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Then follow one of the digestion procedures listed below.

7.2.3.1 Digest the sample using the appropriate method (Method 3010, 3015, or Parr Bomb), using the HF modification and then continuing to follow the procedures described in Section 7.2.1.

7.2.3.2 Combine with the digestate prepared in Section 7.2.1. The resultant combined sample is a Fraction 1 precursor. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 mL (or the appropriate volume for the expected metals concentration) with water. This dilution is Fraction 1. Measure and record the volume of the Fraction 1 solution to within 0.1 mL. Quantitatively remove a 50-mL aliquot and label as Fraction 1B. Label the remaining 250 mL portion as Fraction 1A. Fraction 1A is used for ICP-AES, ICP-MS, or AA analysis for all metals except mercury. Fraction 1B is used for the determination of front-half mercury.

7.2.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 mL. Remove a 75-to 100-mL aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as aliquot Fraction 2A. Aliquot Fraction 2A defines the volume of 2A prior to digestion. All of aliquot Fraction 2A is digested to produce concentrated Fraction 2A. Concentrated Fraction 2A defines the volume of 2A after digestion which is normally 150 mL. Concentrated Fraction 2A is analyzed for all the metals except mercury. The Fraction 2B aliquot should be prepared and analyzed for mercury as described in Section 7.4.7. Fraction 2A shall be pH 2 or lower. If necessary, use concentrated nitric acid to lower Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Acid digestion is performed by using either prescribed digestion techniques of this manual, or the Method 29 procedures.

7.2.5 Container Nos. 5A, 5B, and 5C (Impingers 4, 5, and 6). Keep these samples separate from each other.

7.2.5.1 Measure and record the volumes of 5A and 5B each to within 0.5 mL. Dilute Sample 5C to 500 mL with water. The Samples 5A, 5B, and 5C are referred to respectively as Fractions 3A, 3B, and 3C. Follow the analysis procedures described in Section 7.4.

7.2.5.2 Because the permanganate rinse and water rinse have the capability to recover a high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse (Fraction 3C) may be very small, possibly even insignificantly small. However, as instructed in this method, add the total of any mercury measured in and calculated for the HCl rinse (Fraction 3C) to that for Fractions 1B, 2B, 3A, and 3B for calculation of the total sample mercury concentration.

7.2.6 Container No. 6 (silica gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field).

7.3 Calibration

Refer to the appropriate analytical methods for the proper calibration procedures.

7.4 Sample analysis.

7.4.1 For each sampling train, seven individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front half of the train. Fraction 1A is for ICP-AES and AA analysis as described in Section 7.4.5. Fraction 1B is for determination of front-half mercury as described in Section 7.4.7.

7.4.2 The back half of the train was used to prepare the third through seventh samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the moisture knockout, if used, and HNO_3/H_2O_2 Impingers 1 through 3. Fraction 2A is for ICP-AES or AA analysis. Fraction 2B will be analyzed for mercury.

7.4.3 Samples 5A, 5B, and 5C are labeled Fractions 3A, 3B, and 3C, respectively. They consist of the impinger contents and rinses from the empty Impinger 4 and the permanganate Impingers 5 and 6. These samples are analyzed for mercury as described in Section 7.4.7. The total back-half mercury catch is determined from the sum of Fraction 2B and Fraction 3A, 3B, and 3C.

7.4.4 Initially, analyze all samples for iron, aluminum, and all the target metals except mercury . If iron and aluminum are present in the sample, the sample may have to be diluted so that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic, cadmium, chromium, and lead.

> NOTE: When analyzing samples in a hydrofluoric acid matrix, an alumina torch should be used. Since all front-half samples will contain hydrofluoric acid, use an alumina torch.

7.4.5 ICP-AES analysis. Fraction 1A and Fraction 2A are analyzed by ICP-AES using Method 6010. Refer to Method 6010 for the proper analytical procedures.

7.4.6 AA by direct aspiration and/or graphite furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AA is desired, Table A-2 should also be consulted to determine possible interferences and techniques to use for their minimization. Refer to Vol. 1A of this manual to determine the appropriate analytical protocol.

7.4.7 Cold vapor AA mercury analysis. Fraction 1B, Fraction 2B, and Fraction 3A, 3B, and 3C should be analyzed separately for mercury using cold vapor atomic absorption spectrometry following the method outlined in Method 7470. Refer to Method 7470 for the proper analytical protocol. If no prior knowledge exists of the expected amount of mercury

in the sample, dilute a 1-mL to 10-mL aliquot of each original sample to 100 mL. Record the amount of the aliquot used for dilution to 100 mL. Digest the sample according to Method 7470. To determine the stack emission value for mercury, the amount of the aliquot of the sample used for dilution and analysis is dependent on the amount of mercury in the aliquot: the total amount of mercury in the aliquot used for analysis must be less than 1 ug, and within the range (zero to 1000 ng) of the calibration curve.

7.4.8 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) may be used for analysis of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, As, Tl and Zn. Refer to Method 6020 for the proper analytical procedure.

7.5 Calculations

7.5.1 Dry gas volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

7.5.2 Volume of water vapor and moisture content. Using the data obtained from this test, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

7.5.3 Stack gas velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

7.5.4 Metals (except mercury) in source sample.

7.5.4.1 Fraction 1A, front half, metals (except Hg). Calculate the amount of each metal collected in Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{a1} F_d V_{soln,1} \qquad \text{Eq. } 1^1$$

where:

M_{fh} = total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1), µg.

C_{a1} = concentration of metal in sample Fraction 1A as read from the standard curve (µg/mL).

F_d = dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, when a 2 mL volume of Fraction 1A is diluted to 10 mL, F_d = 5).

$V_{soln,1}$ = total volume of digested sample solution (Fraction 1), mL.

7.5.4.2 Fraction 2A, back half, metals (except Hg). Calculate the amount of each metal collected in Fraction 2 of the sampling train using the following equation.

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. } 2^1$$

[1]If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

where:

M_{bh} = total mass of each metal (except Hg) collected in the back half of the sampling train (Fraction 2), µg.

C_{a2} = concentration of metal in sample concentrated Fraction 2A, as read from the standard curve (µg/mL).

F_a = aliquot factor, volume of Fraction 2 divided by volume of aliquot Fraction 2A. See Section 7.2.4.

V_a = total volume of digested sample solution (concentrated Fraction 2A), mL. See Section 7.2.4.

7.5.4.3 Total train, metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb}) \quad \text{Eq. } 3^1$$

where:

M_t = total mass of each metal (separately stated for each metal) collected in the sampling train, µg.

M_{fhb} = bank correction value for mass of metal detected in front-half field reagent blank, µg.

M_{bhb} = blank correction value for mass of metal detected in back-half field reagent blank, µg.

NOTE: If the measured blank value for the front half (M_{fhb}) is in the range 0.0 to "A" µg [where "A" µg equals the value determined by multiplying 1.4 µg/in.^{2} times the actual area in square inches of the filter used in the emission sample], M_{fhb} may be used to correct the emission sample value (M_{fh}); if M_{fhb} exceeds "A" µg, the greater of the two following values may be used: "A" µg, or the lesser value of M_{fhb} or 5 percent of M_{fh}.

If the measured blank value for the back half (M_{bhb}) is in the range 0.0 to 1 µg, M_{bhb} may be used to correct the emission sample value (M_{bh}); if M_{bhb} exceeds 1 µg, the greater of the two following values may be used: 1 µg or the lesser value of M_{bhb}or 5 percent of M_{bh}.

7.5.5 Mercury in source sample.

7.5.5.1 Fraction 1B, front half, Hg. Calculate the amount of mercury collected in the front half, Fraction 1, of the sampling train using the following equation:

$$Hg_{fh} = \left(\frac{Q_{fh}}{V_{f1B}}\right) \times V_{soln,1} \quad \text{Eq. 4}$$

[1]If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

where:

Hg_{fh} = total mass of mercury collected in the front half of the sampling train (Fraction 1), µg.
Q_{fh} = quantity of mercury in analyzed sample, µg.
$V_{soln,1}$ = total volume of digested sample solution (Fraction 1), mL.
V_{f1B} = volume of Fraction 1B analyzed, mL. See the following Note.

NOTE: V_{f1B} is the actual amount of Fraction 1B analyzed. For example, if 1 mL of Fraction 1B were diluted to 100 mL to bring it into the proper analytical range, and 1 mL of the 100 mL dilution was analyzed, V_{f1B} would be 0.01.

7.5.5.2 Fraction 2B and Fractions 3A, 3B, and 3C, back half, Hg. Calculate the amount of mercury collected in Fraction 2 using Equation 5 and Fractions 3A, 3B, and 3C using Equation 6. Calculate the total amount of mercury collected in the back half of the sampling train using Equation 7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}} \times V_{soln,2} \qquad \text{Eq. 5}$$

where:

Hg_{bh2} = total mass of mercury collected in Fraction 2, µg.
Q_{bh2} = quantity of mercury in analyzed sample, µg.
$V_{soln,2}$ = total volume of Fraction 2, mL.
V_{f2B} = volume of Fraction 2B analyzed, mL (see the following note).

NOTE: V_{f2b} is the actual amount of Fraction 2B analyzed. For example, if 1 mL of Fraction 2B were diluted to 10 mL to bring it into the proper analytical range, and 5 mL of the 10-mL dilution was analyzed, V_{f2b} would be 0.5 mL. Use Equation 6 to calculate separately the back-half mercury for Fractions 3A, 3B, and 3C.

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}} \times V_{soln,3(A,B,C)} \qquad \text{Eq. 6}$$

where:

$Hg_{bh3(A,B,C)}$ = total mass of mercury collected separately in Fractions A, 3B, or 3C, µg.
$Q_{bh3(A,B,C)}$ = quanty of mercury in separately analyzed samples, µg.
$V_{f3(A,B,C)}$ = volume Fraction 3A, 3B, or 3C analyzed, mL (see above and calculate similarly).
$V_{soln,3(A,B,C)}$ = total volume of Fraction 3A, 3B, or 3C, mL.

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \qquad \text{Eq. 7}$$

where:

Hg_{bh} = total mass of mercury collected in the back half of the sampling train, ug.

7.5.5.3 Total train mercury catch. Calculate the total amount of mercury collected in the sampling train using Equation 8.

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \quad \text{Eq. 8}$$

where:

Hg_t = total mass of mercury collected in the sampling train, µg.
Hg_{fhb} = blank correction value for mass of mercury detected in front-half field reagent blank, µg.
Hg_{bhb} = blank correction value for mass of mercury detected in back-half field reagent blank, µg.

NOTE: If the total of the measured blank values ($Hg_{fhb} + Hg_{bhb}$) is in the range of 0 to 6 ug, then the total may be used to correct the emission sample value ($Hg_{fh} + Hg_{bh}$); if it exceeds 6 µg, the greater of the following two values may be used: 6 µg or 5 percent of the emission sample value ($Hg_{fh} + Hg_{bh}$).

7.5.6 Metal concentration of stack gas. Calculate each metal separately for the cadmium, total chromium, arsenic, nickel, manganese, beryllium, cobalt, copper, lead, phosphorus, thallium, silver, barium, zinc, selenium, antimony, and mercury concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_4 (M_t/V_{m(std)}) \quad \text{Eq. 9}$$

where:

C_s = concentration of each metal in the stack gas, mg/dscm.
K_4 = 10^{-3} mg/µg.
M_t = total mass of each metal collected in the sampling train, µg; (substitute Hg_t for M_t for the mercury calculation).
$V_{m(std)}$ = volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

7.5.7 Isokinetic variation and acceptable results. Same as Method 5, Sections 6.11 and 6.12, respectively.

8.0 QUALITY CONTROL

8.1 Sampling Blanks.

Field Reagent Blanks (FRBs). When analyzed, the blank samples in Container Nos. 7 through 12 shall be processed, digested, and analyzed as follows. Digest and process one of the filters from Container No. 12 contents per Section 7.2.1, 100 mL from Container No. 7 per Section 7.2.2, and 100 mL from Container No. 8 per Section 7.2.3. This produces Fraction Blank 1A and Fraction Blank 1B from Fraction Blank 1. (If desired, the other two filters may be digested separately according to Section 7.2.1, diluted separately to 300 mL each, and analyzed separately to produce a blank value for each of the two additional filters. If these analyses are performed, they will produce two additional values for each of Fraction Blank 1A and Fraction Blank 1B. The three Fraction Blank 1A values will be calculated as three values of M_{fhb} in Equation 3 of Section 7.5.4.3, then the three values shall be totalled and divided by three to become the value M_{fhb} to be used in the computation of M_t by Equation 3. Similarly, the three Fraction Blank 1B values will be calculated separately as three values, totalled, averaged, and used as the value for Hg_{fhb} in Equation 8 of Section 7.5.5.3. The analyses of the two extra filters are optional and are not a requirement of this method, but if the analyses are performed, the results must be considered as described above.) Combine 100 mL of Container No. 8A with 200 mL of the contents of Container No. 9 and digest and process the resultant volume per Section 7.2.4. This produces concentrated Fraction Blank 2A and Fraction Blank 2B from Fraction Blank 2. A 100-mL portion of Container No. 8A is Fraction Blank 3A. Combine 100 mL of the contents of Container No. 10 with 33 mL of the contents of Container No. 8B. This produces Fraction Blank 3B. (Use 400 mL as the volume of Fraction Blank 3B when calculating the blank value. Use the actual volumes when calculating all the other blank values). Dilute 225 mL of the contents of Container No. 11 to 500 mL with water. This produces Fraction Blank 3C. Analyze Fraction Blank 1A and Fraction Blank 2A per Section 7.4.5 and/or Section 7.4.6 Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blank 3A, 3B, and 3C per Section 7.4.7. The analysis of Fraction Blank 1A produces the front-half reagent blank correction values for the metals except mercury; the analysis of Fraction Blank 1B produces the front-half reagent blank correction value for mercury. The analysis of Fraction Blank 2A produces the back-half reagent blank correction values for the metals except mercury, while separate analysis of Fraction Blanks 2B and 3 produce the back-half reagent blank correction value for mercury.

8.2 Quality Control Samples. The following quality control samples should be analyzed. All appropriate Chapter One quality control procedures should be followed.

8.2.1 ICP-AES or ICP-MS analysis. Follow the quality control shown in Chapter One and Section 8 of Method 6010 or 6020 as appropriate.

8.2.2 Direct aspiration and/or graphite furnace AA analysis for antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, nickel, manganese, mercury, phosphorus, selenium, silver, thallium, and zinc. All samples should be analyzed in duplicate. Perform a post-digestion spike on at least one front-half sample and one back-half sample or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the post-digestion spike, analyze each sample by the method of standard additions.

8.2.3 Cold vapor AA analysis for mercury. All samples should be analyzed in duplicate. Perform a post-digestion or matrix spike on one sample from the nitric acid impinger portion (must be within 25% or samples must be analyzed by the method of standard additions).

9.0 METHOD PERFORMANCE

9.1 To ensure optimum sensitivity in obtaining the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, on at least one sample (run) in the source test and for each metal analyzed, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition, etc., shall be used to establish the quality of the data.

9.2 Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table 2 for a specific test by using one or more of the following options:

- A 1-hour sampling run collects a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased and 5 m^3 are collected, the in-stack method detection limits would be one fourth of the values shown in Table A-1 (i.e., the method is four times more sensitive than an hour run).

- The in-stack detection limits assume that all of the sample is digested (with exception of the aliquot for mercury) and the final liquid volumes for analysis are 300 mL for the front half (Fraction 1) and 150 mL for the back half (Fraction 2A). If the volume of the front half is concentrated from 300 mL to 30 mL, the front half in-stack detection limits would be one tenth of the values shown above (ten times more sensitive). If the back-half volume is concentrated from 150 mL to 25 mL, the in-stack detection limits would be one sixth of the above values. Matrix effects checks are necessary on analyses of samples and typically are of greater significance for samples that have been concentrated to less than the normal sample volume. Reduction to a volume of less than 25 mL may not allow redissolving of the residue and may increase interference by other compounds.

- When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front and back halves is reduced by factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive).

- Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase detection limits (i.e., the method would be less sensitive). The front-half and back-half samples (Fractions 1A plus 2A) can be combined proportionally prior to analysis. The resultant liquid volume (excluding the mercury fractions, which must be analyzed separately) is recorded. Combining the sample as described does not

allow determination (whether front or back half) of where in the train the sample was captured. The in-stack method detection limit then becomes a single value for all metals except mercury, for which the contribution of the mercury fraction must be considered.

- The above discussion assumes no blank correction.

9.3 Using (1) the procedures described in this method, (2) the analytical detection limits listed in Section 1, (3) a volume of 300 mL for the front half and 150 mL for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3, the corresponding in-stack method detection limits are presented in Table A-2 and calculated as shown:

$$\frac{A \times B}{C} = D$$

where:

A = analytical detection limit, µg/mL.
B = volume of sample prior to aliquot for analysis, mL.
C = stack sample volume, dscm (dsm^3).
D = in-stack detection limit, $\mu g/m^3$.

Values in Table A-2 are calculated for the front and back half and/or the total train.

10.0 REFERENCES

1. Method 303F, Standard Methods for the Examination of Water Wastewater, available from the American Public Health Association, 1015 18th Street, N.W., Washington, D.C. 20036.

2. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C.

3. EPA Methods 1 through 5, 12, and 29 Code of Federal Regulations, Title 40, Part 60, Appendix A.

4. ASTM Standard Method D2986-71, available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

TABLE 2. IN-STACK METHOD DETECTION LIMITS (µg/m^3)
FOR TRAIN FRACTIONS USING ICP-AES AND AA

Metal	Front Half Fraction 1 Probe and Filter	Back Half Fraction 2 Impingers 1-3	Back Half Fraction 3 Impingers 4-5	Total Train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Cobalt	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3)*
Mercury	0.6**	3.0**	2.0**	5.6**
Nickel	3.6	1.8		5.4
Phosphorus	18.0	9.0		27.0
Selenium	18.0 (0.5)*	9.0 (0.3)*		27.0 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

( )* Detection limit when analyzed by GFAA.
** Detection limit when analyzed by CVAA, estimated for back-half and total train.

NOTE: Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

TABLE 3. APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AA ANALYSIS

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Sb	Aspiration	7040	217.6	1000 mg/mL Pb Ni, Cu, or acid	Use secondary wavelength of 231.1 nm. Match sample & standards acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
As	Furnace	7060	193.7	Arsenic vola-tilization Aluminum	Spiked samples & add nickel nitrate solution to digestates prior to analyses Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium Barium ionization	High hollow cathode current & narrow band set 2 mL of KCl per 100 mL of sample
Be	Aspiration	7090	234.9	500 ppm Al High Mg & Si	Add 0.1% fluoride Use method of standard additions
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects
Cd	Aspiration	7130	228.8	Absorption & light scattering	Background correction is required
Cd	Furnace	7131	228.8	As above Excess chloride Pipet tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips

(continued)

TABLE 3 (CONTINUED)

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Cr	Aspiration	7190	357.9	Alkali metal Absorption & scattering	KCl ionization suppressant in sample & standard Consult manufacturer's literature
Cr	Furnace	7191	357.9	200 mg/L calcium & phosphate	All calcium nitrate for a known constant effect and to eliminate effect of phosphate
Cu	Aspiration	7210	324.7	Absorpt & scatter	Consult manufacturer's manual
Fe	Aspiration	7380	283.3	Contamination	Great care taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternative	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 uL of phosphorus acid to 1-mL of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternative	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternative Fe, Co, & Cr Nonlinear response	Background correction required Matrix matching or a nitrous-oxide/acetyl flame Sample dilution or use 352.4 nm line

(continued)

TABLE 3 (CONTINUED)

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Se	Furnace	7740	196.0	Volatility	Spike samples & reference materials & add nickel nitrate to minimize volatilization
				Adsorpt & scatter	Background correction is required & Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Absorpt & scatter	Background correction is required
				AgCl insoluble	Avoid hydrochloric acid unless silver is in solution as a chloride complex
				Viscosity	Sample & standards monitored for aspiration rate
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used
Tl	Furnace	7841	276.8		Background correction is required
				Hydrochloric acid or chloride	Verify that losses are not occurring for volatization by spiked samples or standard additions Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu & P	Strontium removes Cu and phosphate
				Contamination	Care should be taken to avoid contamination

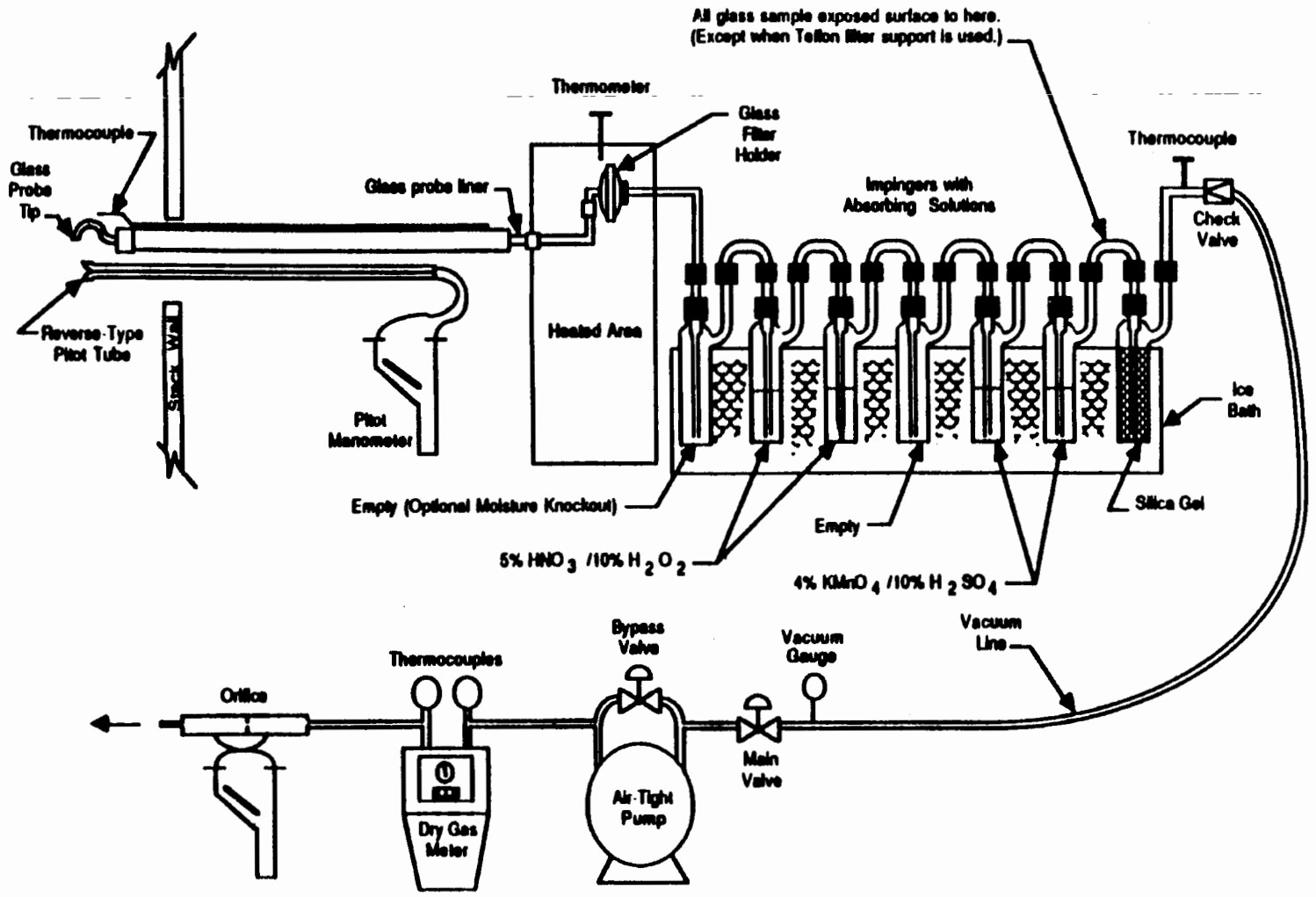
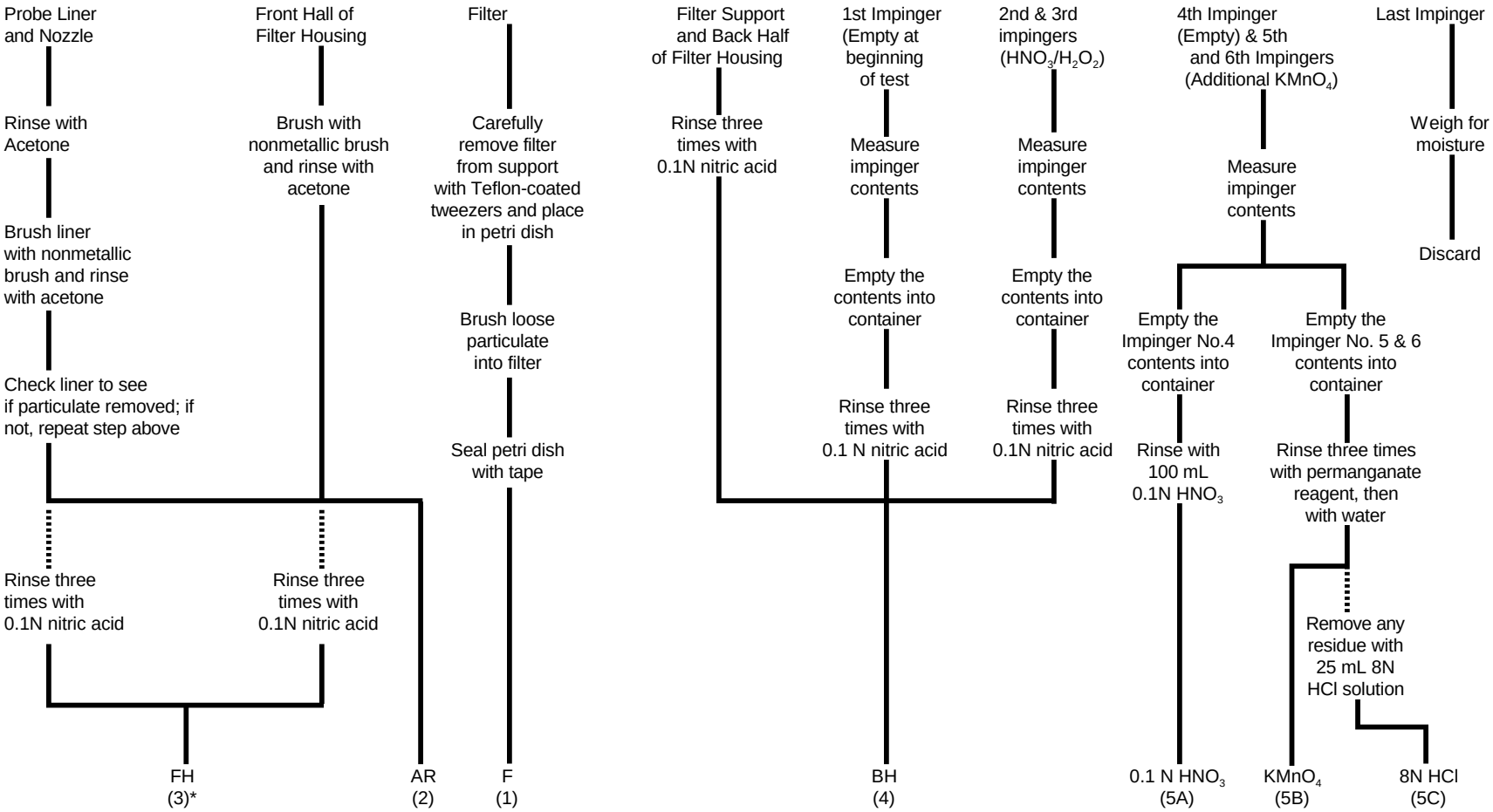


FIGURE 1. SCHEMATIC OF MULTIPLE METALS SAMPLING TRAIN CONFIGURATION



* Number in parentheses indicates container number

FIGURE 2. SAMPLE RECOVERY SCHEME

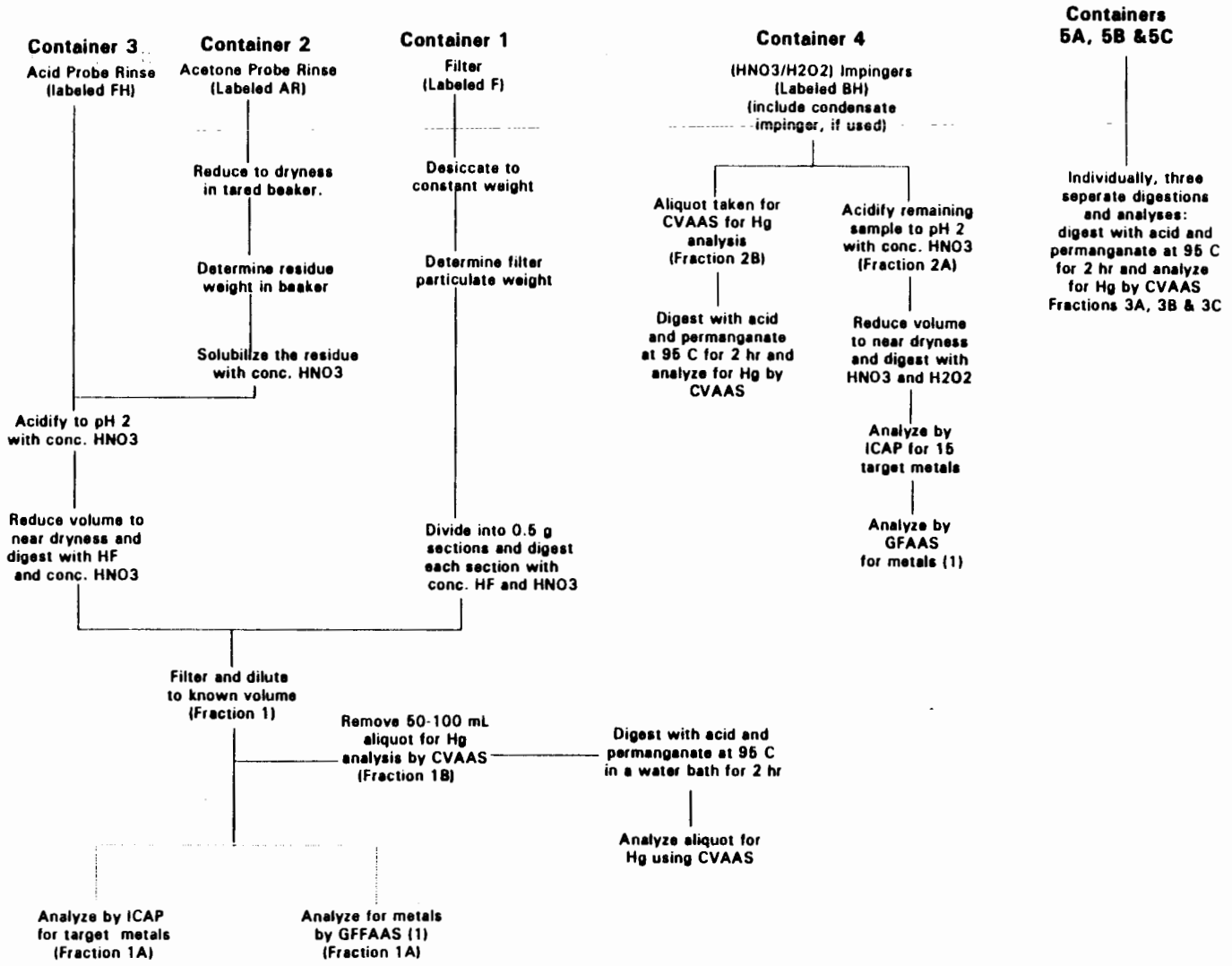
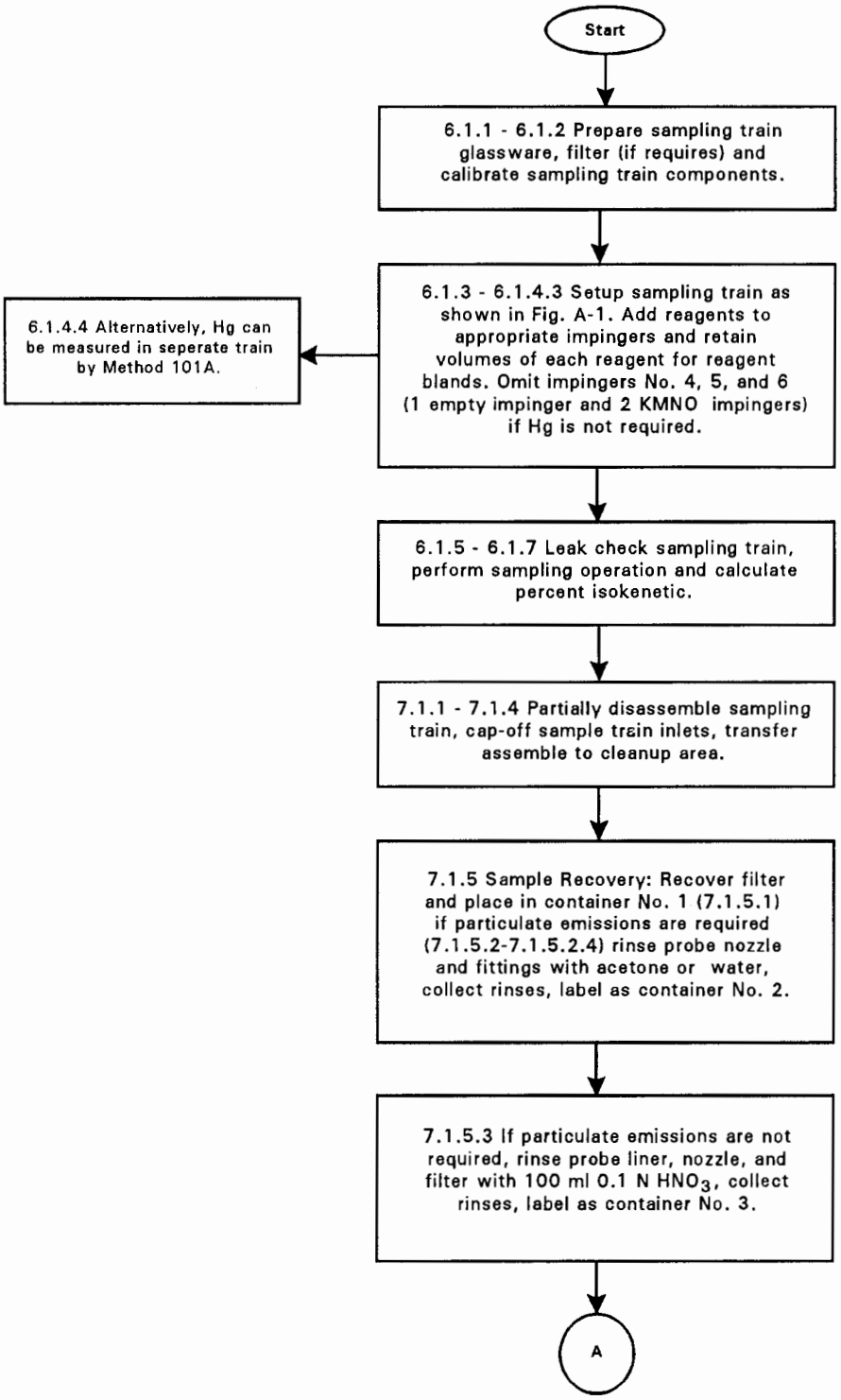
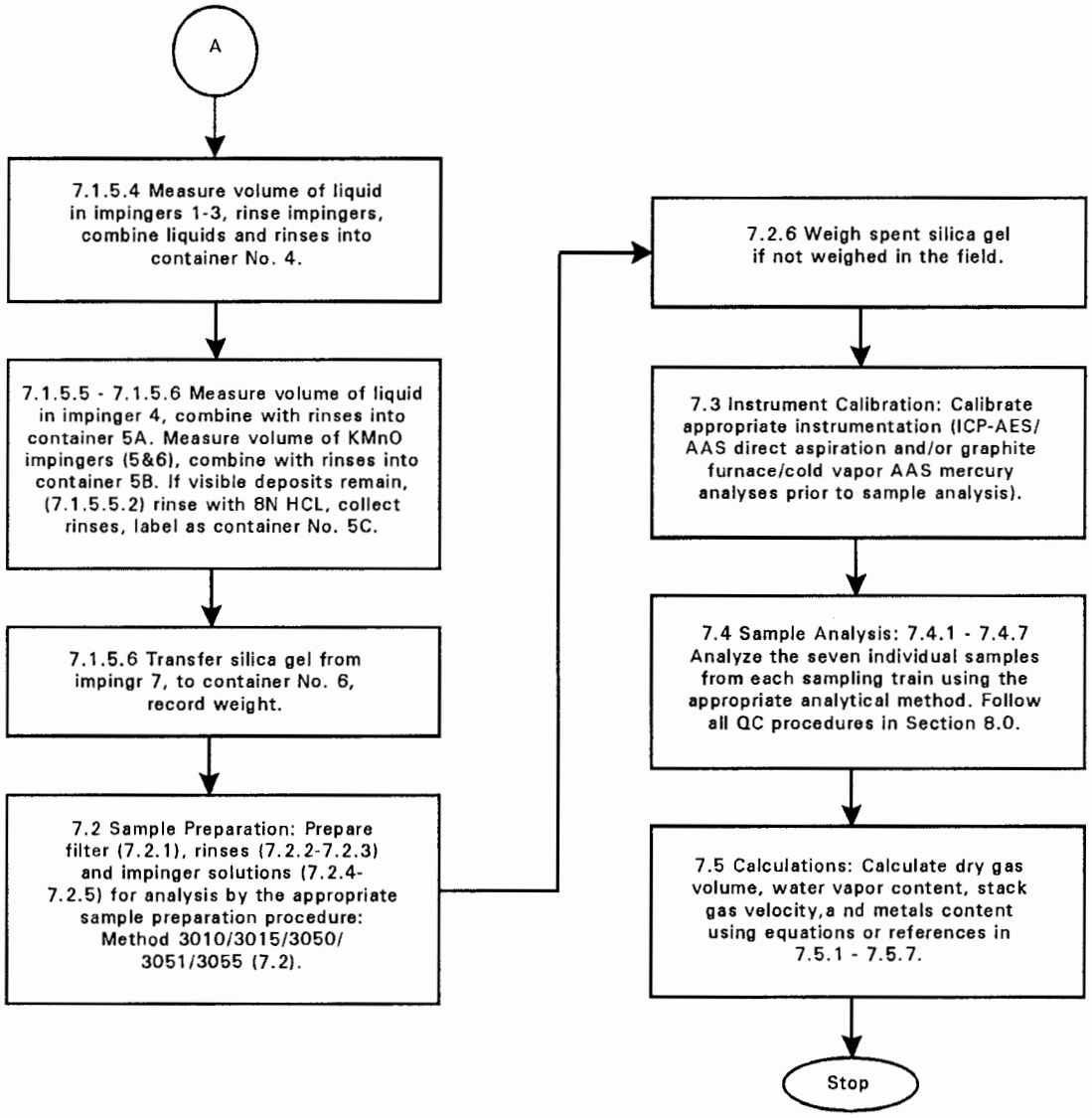


FIGURE 3. SAMPLING PREPARATION AND ANALYSIS SCHEME


Start
6.1.1 - 6.1.2 Prepare sampling train glassware, filter (if requires) and calibrate sampling train components.
6.1.3 - 6.1.4.3 Setup sampling train as shown in Fig. A-1. Add reagents to appropriate impingers and retain volumes of each reagent for reagent blands. Omit impingers No. 4, 5, and 6 (1 empty impinger and 2 KMNO impingers) if Hg is not required.
6.1.4.4 Alternatively, Hg can be measured in seperate train by Method 101A.
6.1.5 - 6.1.7 Leak check sampling train, perform sampling operation and calculate percent isokenetic.
7.1.1 - 7.1.4 Partially disassemble sampling train, cap-off sample train inlets, transfer assemble to cleanup area.
7.1.5 Sample Recovery: Recover filter and place in container No. 1 (7.1.5.1) if particulate emissions are required (7.1.5.2-7.1.5.2.4) rinse probe nozzle and fittings with acetone or water, collect rinses, label as container No. 2.
7.1.5.3 If particulate emissions are not required, rinse probe liner, nozzle, and filter with 100 ml 0.1 N HNO_3, collect rinses, label as container No. 3.
A


A
7.1.5.4 Measure volume of liquid in impingers 1-3, rinse impingers, combine liquids and rinses into container No. 4.
7.1.5.5 - 7.1.5.6 Measure volume of liquid in impinger 4, combine with rinses into container 5A. Measure volume of KMnO impingers (5&6), combine with rinses into container 5B. If visible deposits remain, (7.1.5.5.2) rinse with 8N HCL, collect rinses, label as container No. 5C.
7.1.5.6 Transfer silica gel from impingr 7, to container No. 6, record weight.
7.2 Sample Preparation: Prepare filter (7.2.1), rinses (7.2.2-7.2.3) and impinger solutions (7.2.4-7.2.5) for analysis by the appropriate sample preparation procedure: Method 3010/3015/3050/ 3051/3055 (7.2).
7.2.6 Weigh spent silica gel if not weighed in the field.
7.3 Instrument Calibration: Calibrate appropriate instrumentation (ICP-AES/ AAS direct aspiration and/or graphite furnace/cold vapor AAS mercury analyses prior to sample analysis).
7.4 Sample Analysis: 7.4.1 - 7.4.7 Analyze the seven individual samples from each sampling train using the appropriate analytical method. Follow all QC procedures in Section 8.0.
7.5 Calculations: Calculate dry gas volume, water vapor content, stack gas velocity,a nd metals content using equations or references in 7.5.1 - 7.5.7.
Stop

METHOD 0061

DETERMINATION OF HEXAVALENT CHROMIUM EMISSIONS
FROM STATIONARY SOURCES

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of hexavalent chromium (Cr^{+6}) emissions from hazardous waste incinerators, municipal waste incinerators, municipal waste combustors, and sewage sludge incinerators. With the approval of the Administrator, this method may also be used to measure total chromium. The sampling train, constructed of Teflon components, has only been evaluated at temperatures of less than 300°F. Trains constructed of other materials, for testing at higher temperatures, are currently being evaluated.

1.2 Range: If employing a preconcentration procedure, the lower limit of the detection range can be extended to 16 nanograms per dry standard cubic meter (ng/dscm) with a 3 dscm gas sample (0.1 ppb in solution). With sample dilution, there is no upper limit. Follow your manufacturer's specific instructions on employing the preconcentration procedure for these analyses.

2.0 SUMMARY OF METHOD

2.1 For incinerators and combustors, the Cr^{+6} emissions are collected isokinetically from the source: To eliminate the possibility of Cr^{+6} reduction between the nozzle and impinger, the emission samples are collected with a recirculatory train where the impinger reagent is continuously recirculated to the nozzle. Recovery procedures include a post-sampling purge and filtration. The impinger train samples are analyzed for Cr^{+6} by an ion chromatograph equipped with a post-column reactor and a visible wavelength detector. The IC/PCR separates the Cr^{+6} as chromate ($CrO_4^{=}$) from other diphenylcarbazide reactions that occur in the post-column reactor. To increase sensitivity for trace levels of chromium, a preconcentration system may also be used in conjunction with the IC/PCR.

3.0 INTERFERENCES

3.1 Components in the sample matrix may cause Cr^{+6} to convert to trivalent chromium (Cr^{+3}) or cause Cr^{+3} to convert to Cr^{+6}. A post-sampling nitrogen purge and sample filtration are included to eliminate many of these interferences.

3.2 The chromatographic separation of Cr^{+6} using ion chromatography reduces the potential for other metals to interfere with the post-column reaction. For the IC/PCR analysis, only compounds that coelute with Cr^{+6} and affect the diphenylcarbazide reaction will cause interference.

3.3 Sample cross-contamination that can occur when high-level and low-level samples or standards are analyzed alternately is eliminated by thorough purging of the sample loop. Purging can easily be obtained by increasing the injection volume of the samples to ten times the size of the sample loop.

4.0 APPARATUS

4.1 Sampling Train: Schematics of the recirculatory sampling trains employed in this method are shown in Figures 1 and 2. The recirculatory train is readily assembled from commercially available components. All portions of the train in contact with the sample are either glass, quartz, Tygon, or Teflon, and are to be cleaned as per Section 6.0. The metering system is identical to that specified by Method 5; the sampling train consists of the following components:

4.1.1 Probe Nozzle: Glass or Teflon with a sharp, tapered leading edge. The angle of taper shall be $\leq 30^{\circ}$ and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to ½ in.) -- or larger if higher volume sample trains are used -- inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 7.1.1.

4.1.2 Teflon Aspirator or Pump/Sprayer Assembly (see Figures 1 and 2): Teflon aspirator capable of recirculating absorbing reagent at 50 mL/min while operating at 0.75 cfm. Alternatively, a pump/sprayer assembly may be used instead of the Teflon aspirator. A Teflon union-T is connected behind the nozzle to provide the absorbing reagent/sample gas mix; a peristaltic pump is used to recirculate the absorbing reagent at a flow rate of at least 50 mL/min. Teflon fittings, Teflon ferrules, and Teflon nuts are used to connect a glass or Teflon nozzle, recirculation line, and sample line to the Teflon aspirator or union-T. Tygon, C-flex or other suitable inert tubing for use with peristaltic pump.

4.1.3 Teflon Sample Line: Teflon, 3/8" ID, of suitable length to connect aspirator (or T-union) to first Teflon impinger.

4.1.4 Teflon Recirculation Line: Teflon, 1/4" O.D. and 1/8" I.D., of suitable length to connect first impinger to aspirator (or T-union).

4.1.5 Teflon Impingers: Four Teflon impingers; Teflon tubes and fittings, such as made by Savillex*, can be used to construct impingers 2" diameter by 12" long, with vacuum-tight 3/8" O.D. Teflon compression fittings. Alternatively, standard glass impingers that have been Teflon-lined, with Teflon stems and U-tubes, may be used. Inlet fittings on impinger top to be bored through to accept 3/8" O.D. tubing as impinger stem. The second and third 3/8" OD Teflon stem has a 1/4" OD Teflon tube, 2" long, inserted at its impinger stem should extend to 2" from impinger bottom, high enough in the impinger reagent to prevent air from entering recirculating line; the second and third impinger stems should extend to ½" from impinger bottom. The first impinger should include a 1/4" O.D. Teflon compression fitting for recirculation line. The fourth impinger serves as a knockout impinger to trap solution carried over from the previous impingers.

NOTE: Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

4.1.6 Glass Impinger: Silica gel impinger, Vacuum-tight impingers, capable of containing 400 g. of silica gel, with compatible fittings. The silica gel impinger will have a modified stem (½" ID at tip of stem).

4.1.7 Thermometer, (identical to that specified by Method 5) at the outlet of the silica gel impinger, to monitor the exit temperature of the gas.

4.1.8 Metering System, Barometer, and Gas Density Determinations Equipment: Same as Method 0010.

4.2 Sample Recovery: Clean all items for sample handling or storage with 10% nitric acid solution by soaking, where possible, and rinse thoroughly with reagent water before use.

4.2.1 Nitrogen Purge Line: Inert tubing and fittings capable of delivering 0 to 1 scf/min (continuously adjustable) of nitrogen gas to the impinger train from a standard gas cylinder (see Figure 3).

4.2.2 Wash Bottles: Two polyethylene wash bottles, for reagent water-nitric rinse solution.

4.2.3 Sample Storage Containers: Polyethylene, with leak-free screw cap, 500-mL or 1000-mL.

4.2.4 1000-mL Graduated Cylinder and Balance.

4.2.5 Plastic Storage Containers: Air tight containers to store silica gel.

4.2.6 Funnel and Rubber Policeman: To aid in transfer of silica gel from impinger to storage container; not necessary if silica gel is weighed directly in the impinger.

4.3 Sample Preparation for Analysis: Sample preparation prior to analysis includes purging the sample train immediately following the sample run, and filtering the recovered sample to remove particulate matter immediately following recovery.

4.3.1 Beakers, Funnels, Volumetric Flasks, Volumetric Pipets, and Graduated Cylinders: Assorted sizes, Teflon or glass, for preparation of samples, sample dilution, and preparation of calibration standards. Prepare initially following procedure described in Section 5.1.3 and rinse between use with 0.1 M HNO_3 and reagent water.

4.3.2 Filtration Apparatus: Teflon, or equivalent, for filtering samples, and Teflon filter holder. Teflon impinger components have been found to be satisfactory as a sample reservoir for pressure filtration using nitrogen.

4.4 Ion Chromatograph: Refer to Section 4.0 of Method 7199 for instrument and equipment specifications.

4.4.1 Preconcentrator: System in-line with the ion chromatograph.

OR

4.5 Sample preconcentration system: A high performance ion chromatograph (HPIC) non-metallic column with acceptable anion retention characteristics and sample loading rates as described in the analytical method.

5.0 REAGENTS

5.1 All inorganic reagents should conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. All prepared reagents should be checked by IC/PCR analysis for Cr^{+6} to assure that contamination is below the analytical detection limit for direct injection or, if selected, preconcentration. If total chromium is also to be determined, the reagents should also be checked by the analytical technique selected to assure that contamination is below the analytical detection limit.

5.2 Sampling.

5.2.1 Reagent water: Reagent water shall be interferences free. All references to water in the method refer to reagent water unless otherwise specified. A definition of reagent water can be found in Chapter One.

5.2.2 Potassium Hydroxide, 0.1 M: Add 5.6 gm of KOH(s) to approximately 900 mL of reagent water and let dissolve. Dilute to 1000 mL with reagent water. A brief unpublished EPA study showed sources of 2N KOH with concentrations of hexavalent chromium ranging from 1.02 ppb to 7.86 ppb. If the lowest detection limit is needed for a given project, an effort should be made to obtain KOH with the minimum possible contamination. Initial attempts to develop an acceptable purification procedure have been unsuccessful.

NOTE: At sources with high concentrations of acids and/or SO_2, the concentration of KOH should be increased to 0.5 M to insure that the pH of the solution is above 8.5 after sampling.

5.2.3 Silica Gel and Crushed Ice: Same as Method 5.

5.3 Sample Recovery: The reagents used in sample recovery are as follows:

5.3.1 Water: Same as Section 5.2.1.

5.3.2 Nitric Acid, 0.1 M: Add 6.3 mL of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 mL of reagent water. Dilute to 1000 mL with reagent water, and mix well.

5.3.3 pH Indicator Strip: pH indicator capable of determining pH of solution between the pH range of 7 and 12, at 0.5 pH intervals.

5.4 Sample Preparation

5.4.1 Reagent water: Same as Section 5.2.1.

5.4.2 Nitric Acid, 0.1 M: Same as Section 5.3.2.

5.4.3 Filters: Acetate membrane, or equivalent, filters with 0.45 micrometer or smaller pore size to remove insoluble material.

5.5 Analysis

5.5.1 Refer to Section 5.0 of Method 7199 for instruction on preparation of analytical reagents.

5.6 Performance Audit Sample: A performance audit sample should be analyzed in conjunction with the samples. The audit sample should be prepared in a suitable sample matrix at a concentration similar to the actual field samples.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Section 6.0 of Method 7199 for the proper procedures when collecting, preserving, and handling samples.

6.2 If sample preconcentration is used, dropwise addition of the ammonium sulfate/ammonium hydroxide buffer may not be appropriate, since the added sulfate may lead to premature overloading of the column.

6.3 A holding time of 14 days is appropriate for samples collected by Method 0061, even though Method 7199 has a 24 hr. hold for other samples. The Method 0061 samples are already stabilized in an alkaline solution, as opposed to many samples from other media which may be submitted for analysis in an unstable condition. An optional method of demonstrating stability is to field spike some of the sample matrix with known amounts of Cr^{+6} and determine recovery.

7.0 PROCEDURE

CAUTION: Wear Safety Glasses At All Times During This Test Method.

7.1 Sampling: The complexity of this method is such that to obtain reliable results, testers should be trained and experienced with test procedures.

7.1.1 Sample Train Calibration: Calibrate the sample train components according to the indicated sections of Method 5: Probe Nozzle; Pitot Tube; Metering System; Temperature Gauges; Leak-Check of the Metering System; and Barometer.

7.1.2 Pretest Preparation: All components shall be maintained and calibrated according to the procedures described in APTD-0576, unless otherwise specified herein. Rinse all sample train components from the glass nozzle up to the silica gel impinger and sample containers with hot tap water followed by washing with hot soapy water. Next, rinse the train components and sample containers three times with tap water followed by three rinses with reagent water. All the components and container should then be soaked overnight, or a minimum of 4 hours, in a 10 % (v/v) nitric acid solution, then rinsed three times with reagent water. Allow the components to air dry prior to covering all openings with Parafilm, or equivalent.

7.1.3 Preliminary Determinations: Same as Method 5, Section 4.

7.1.4 Preparation of Sampling Train: Measure 300 mL of 0.1 M KOH into a graduated cylinder (or tare-weighed precleaned polyethylene container). Place approximately 140 mL of the 0.1 M KOH reagent in the first Teflon impinger. Split the rest of the 0.1 M KOH between the second and third Teflon impingers. The next Teflon impinger is left dry. Place a preweighed 200-to 400-g portion of indicating silica gel in the final glass impinger. (For sampling periods in excess of two hours, or for high moisture sites, 400-g of silica gel is recommended). Retain reagent blanks of the 0.1 M KOH equal to the volumes used with the field samples.

7.1.5 Leak-Check Procedures: Follow the leak-check procedures given in Method 5: Pretest Leak-Check, Leak-Checks During the Sample Run, and Post-Test Leak-Checks.

7.1.6 Sampling Train Operation: Follow the procedures given in Method 5, Section 4.1.5. If the sampling train should be iced down with water and ice to insure heat transfer with the Teflon impingers.

NOTE: If the gas to be sampled is above 200°F, it may be necessary to wrap three or four feet of the Teflon sample and recirculating lines inside the ice bath to keep the recirculated reagent cool enough so it does not turn to steam.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5. At the end of the sampling run, determine the pH of the reagent in the first impinger using a pH indicator strip. The pH of the solution shall be greater than 8.5. If the pH is not above 8.5, discard the solution. Prepare a clean sampling train as described above using 0.5 M KOH instead of 0.1 M KOH, as noted in Section 5.2.2. For use of the train at relatively high acid sources, it may be necessary to employ extra caustic, stronger caustic, shorter sampling times, and closer monitoring of pH. See the references for suggestions. Leak-check and operate the sampling train as described above. Repeat the sampling run.

7.1.7 Calculation of Percent Isokinetic: Same as Method 5, Section 4.

7.2 Post-test Nitrogen Purge. The nitrogen purge is used as a safeguard against the conversion of hexavalent chromium to the trivalent oxidation state. The purge is effective in the removal of SO_2 from the impinger contents. Attach the nitrogen purge line to the input of the impinger train. Check to insure the output of the impinger train is open, and that the recirculating line is capped off. Open the nitrogen gas flow slowly and adjust the delivery rate to 10 L/min. Check the recirculating line to insure that the pressure is not forcing the impinger reagent out through this line. Continue the purge under these conditions for one-half hour periodically checking the flow rate.

7.3 Sample Recovery: Begin cleanup procedures as soon as the train assembly has been purged at the end of the sampling run. The probe assembly may be disconnected from the sample train prior to sample purging. The probe assembly should be allowed to cool prior to sample recovery. Disconnect the umbilical cord from the sample train. When the probe assembly can be safely handled, wipe off all external particulate matter near the tip of the nozzle, and cap the nozzle prior to transporting the sample train to a clean up area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions.

7.3.1 Container No. 1 (Impingers 1 through 3): Disconnect the first impinger from the second impinger and disconnect the recirculation line form the aspirator or peristaltic pump. Drain the Teflon impingers into a precleaned graduated cylinder or tare-weighted precleaned polyethylene sample container and measure the volume of the liquid to within 1 mL or 1 gm. Record the volume of liquid present as this information is required to calculate the moisture content of the flue gas sample. If necessary, transfer the sample from the graduated cylinder to a precleaned polyethylene sample container. With reagent water, rinse four times the insides of the glass nozzle, the aspirator, the sample and recirculation lines, the impingers, and the connecting tubing, and combine the rinses with the impinger solution in the sample container.

7.3.2 Container No. 2 (HNO_3 rinse optional for total chromium): With 0.1 M HNO3, rinse three times the entire train assembly, from the nozzle to the fourth impinger, and combine the rinses into a separate precleaned polyethylene sample container for possible total chromium analysis. Repeat the rinse procedure a final time with reagent water, and discard the water rinses. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

7.3.3 Container No. 3 (Silica Gel): Note the color of the indicating silica gel to determine if it has been completely spent. Quantitatively transfer the silica gel from its impinger to the original container, and seal the container. A funnel and a rubber policeman may be used to aid in the transfer. The small amount of particulate that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or the silica gel plus impinger) to the nearest 0.5 g.

7.3.4 Container No 4 (0.1 M KOH Blank): Once during each field test, place a volume of reagent equal to the volume placed in the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

7.3.5 Container No. 5 (Reagent Water Blank): Once during each field test, place a volume of reagent water equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

7.3.6 Container No. 6 (0.1 M HNO_3 Blank): Once during each field test if total chromium is to be determined, place a volume of 0.1 M HNO_3 reagent equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

7.4 Sample Preparation: For determination of Cr^{+6}, the sample should be filtered immediately following recovery to remove any insoluble matter. Nitrogen gas may be used as a pressure assist to the filtration process (see Figure 4). Filter the entire impinger sample through a 0.45 micrometer acetate filter (or equivalent), and collect the filtrate in a 1000-mL graduated cylinder. Rinse the sample container with reagent water three separate times and pass these rinses through the filter, and add the rinses to the sample filtrate. Rinse the Teflon reservoir with reagent water three separate times and pass these rinses through the filter, and add the rinses to the sample. Determine the final volume of the filtrate and rinses and return them to the rinsed polyethylene sample container. Label the container clearly to identify its contents. Rinse the Teflon reservoir once with 0.1 M HNO_3 and once with reagent water and discard these rinses. If total chromium is to be determined, quantitatively recover the filter and residue and place them in a vial. (The acetate filter may be digested with 5 mL of 70% nitric acid; this digestion solution may then be diluted with reagent water for total chromium analysis by inductively coupled plasma atomic emission or graphite furnace atomic absorption spectrometric methods.)

NOTE: If the source has a large amount of particulate in the effluent stream, testing teams may wish to filter the sample twice, once through a 2-5 micrometer filter, then through the 0.45 micrometer filter.

7.4.1 Container No. 2 (HNO_3 rinse, optional for total chromium): This sample shall be analyzed in accordance with the selected procedure for total chromium analysis. At a minimum, the sample should be subjected to a digestion procedure sufficient to solubilize all chromium present.

7.4.2 Container 3 (Silica Gel): Weigh the spent silica gel to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

7.5 Sample Analysis: The Cr^{+6} content of the sample filtrate is determined by ion chromatography coupled with a post column reactor (IC/PCR). Method 7199 should be used for this analysis. To increase sensitivity for trace levels of chromium, a preconcentration system is also used in conjunction with the IC/PCR. Prior to preconcentration and/or analysis, all field samples will be filtered through a 0.45 µm filter. This filtration should be conducted just prior to sample injection/analysis.

7.5.1 Preconcentration: The preconcentration is accomplished by selectively retaining the analyte on a solid absorbent, followed by removal of the analyte from the absorbent.

Refer to Section 7.0 of Method 7199 for the proper sample analysis protocol.

7.6 Calculations

7.6.1 Dry Gas Volume: Using the data form the test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Method 5.

7.6.2 Volume of Water Vapor and Moisture Content: Using the data form the test, calculate $V_{w(std)}$ and B_{ws}, the volume of water vapor and the moisture content of the stack gas, respectively, using Equations 5-2 and 5-3 of Method 5.

7.6.3 Stack Gas Velocity: Using the data form the test and Equations 2-9 of Method 2, calculate the average stack gas velocity.

7.6.4 Total µg Cr^{+6} Per Sample. Calculate as described below:

$$m = (S-B) \times V_{ls} \times d$$

Where:

m = Mass of Cr^{+6} in the sample, µg,
S = Concentration of Sample, µg Cr^{+6}/mL,
B = Concentration of blank, µg Cr^{+6}/mL,
V_{ls} = Volume of sample after filtration, mL, and,
d = Dilution factor (1 if not diluted).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate quality control procedures.

9.0 METHOD PERFORMANCE

9.1 Sensitivity: A minimum detection limit of 8 ng/dscm with a 3 dscm gas sample can be achieved by preconcentration (0.05 ppb in solution). Follow instrument manufacturers instructions for sample preconcentration.

9.2 Precision: The precision of the IC/PCR with sample preconcentration is 5 to 10 percent. The overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr^{+6} and 3.5 ug/dscm of total chromium is 25% and 9% for Cr^{+6} and total chromium, respectively; for hazardous waste incinerators emitting 300 ng/dscm of Cr^{+6} it is 20%.

9.3 Refer to Section 9.0 of Method 7199 for additional analytical method performance information.

10.0 REFERENCES

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2. Steinsberger, S.C., DeWees, W.G., Bell, A.C., Finken, R.A., Knoll, J.E., Midget, M.R. "Development and Validation of the US EPA Hexavalent Chromium Source Emissions Measurement Method," *Fuel Processing Technology* 39 ,pp.265-276 (1994).

3. Steinsberger, S.C., Carver, A.C., DeWees, W.G., Knoll, J.E., Butler, F.E., Midget, M.R. "Sampling and Analytical Methods for Measurement of Low Levels of Hexavalent Chromium from Stationary Sources," *Proceedings of the 1989 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, Air & Waste Management Association, Pittsburgh, PA, 1989, pp.308-313.

4. Knoll, J.E., Midget, M.R., Carver, A.C., Steinsberger, S.C., DeWees, W.G. "Development of a Source Test Method for Hexavalent Chromium," *Proceedings of the 1990 EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, Air & Waste Management Association, Pittsburgh, PA, 1990, pp.579-585.

5. Rom, J.J., "Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment" *APTD-0576*, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1972.

6. US EPA Method 5, *Code of Federal Regulations, Title 40, Part 60, Appendix A*, U.S. Government Printing Office, Washington, DC, 1993.

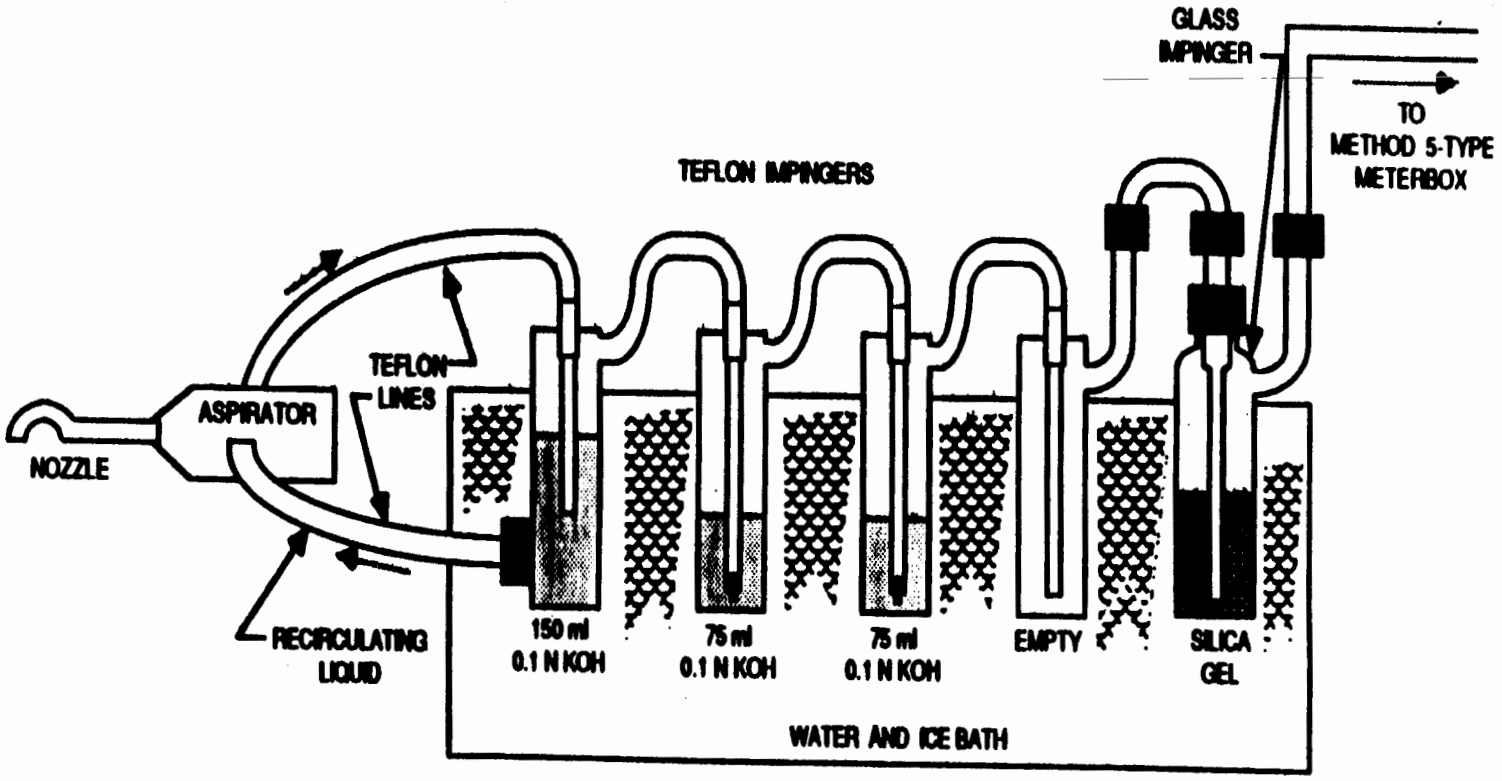


FIGURE 1. TEFLON IMPINGERS - SCHEMATIC OF RECIRCULATORY IMPINGER TRAIN WITH ASPIRATOR ASSEMBLY.

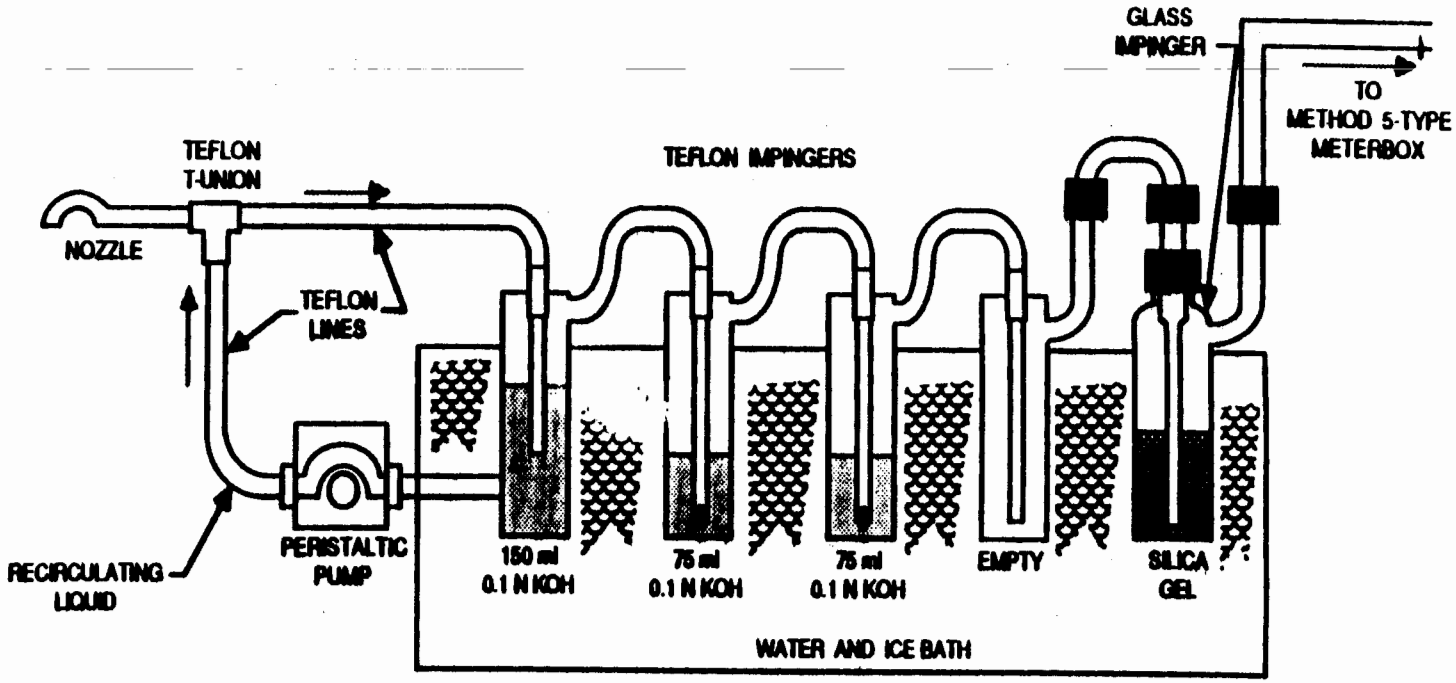


FIGURE 2. TEFLON IMPINGERS - SCHEMATIC OF RECIRCULATORY IMPINGER TRAIN WITH PUMP/SPRAYER ASSEMBLY.

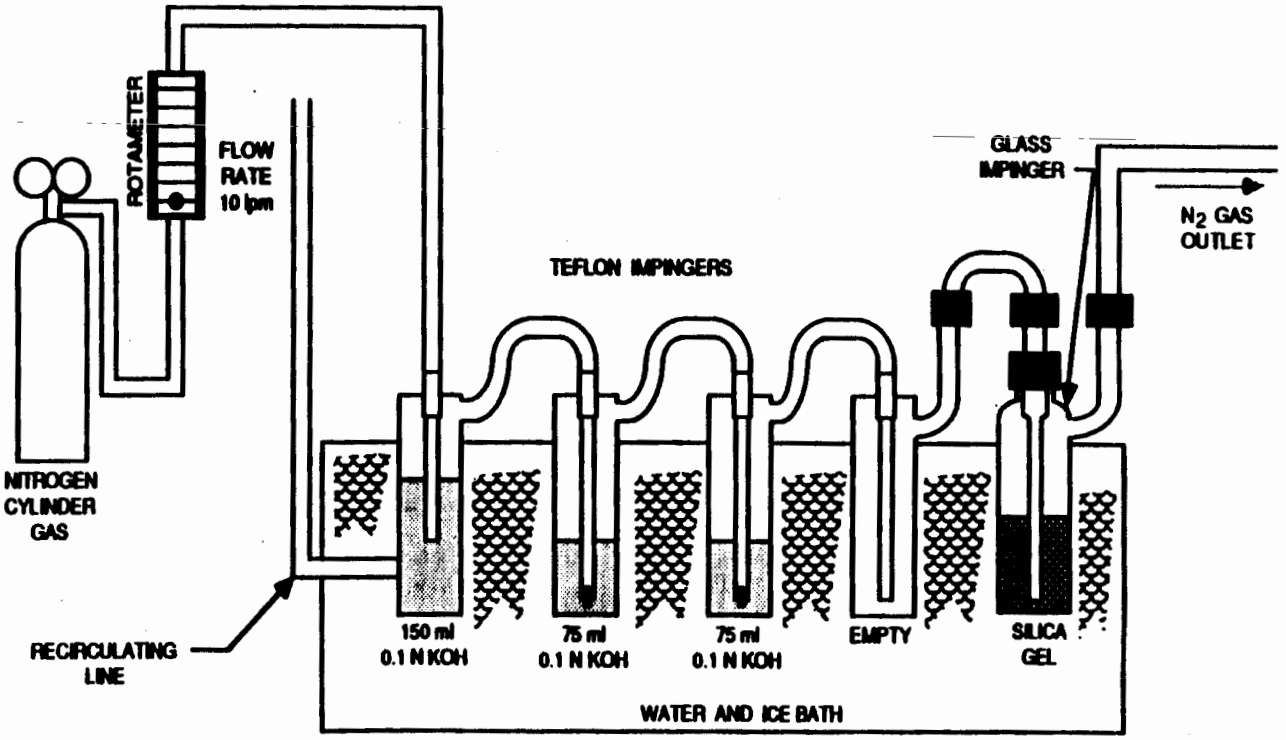


FIGURE 3. TEFLON IMPINGERS - SCHEMATIC OF POST TEST NITROGEN PURGE SYSTEM

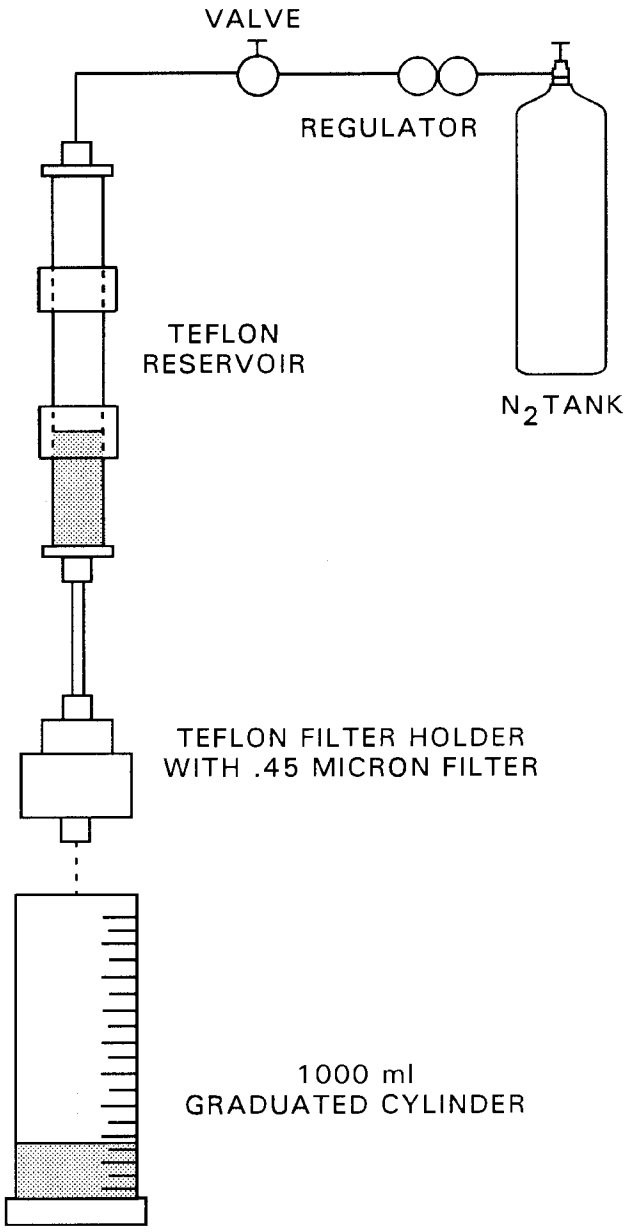
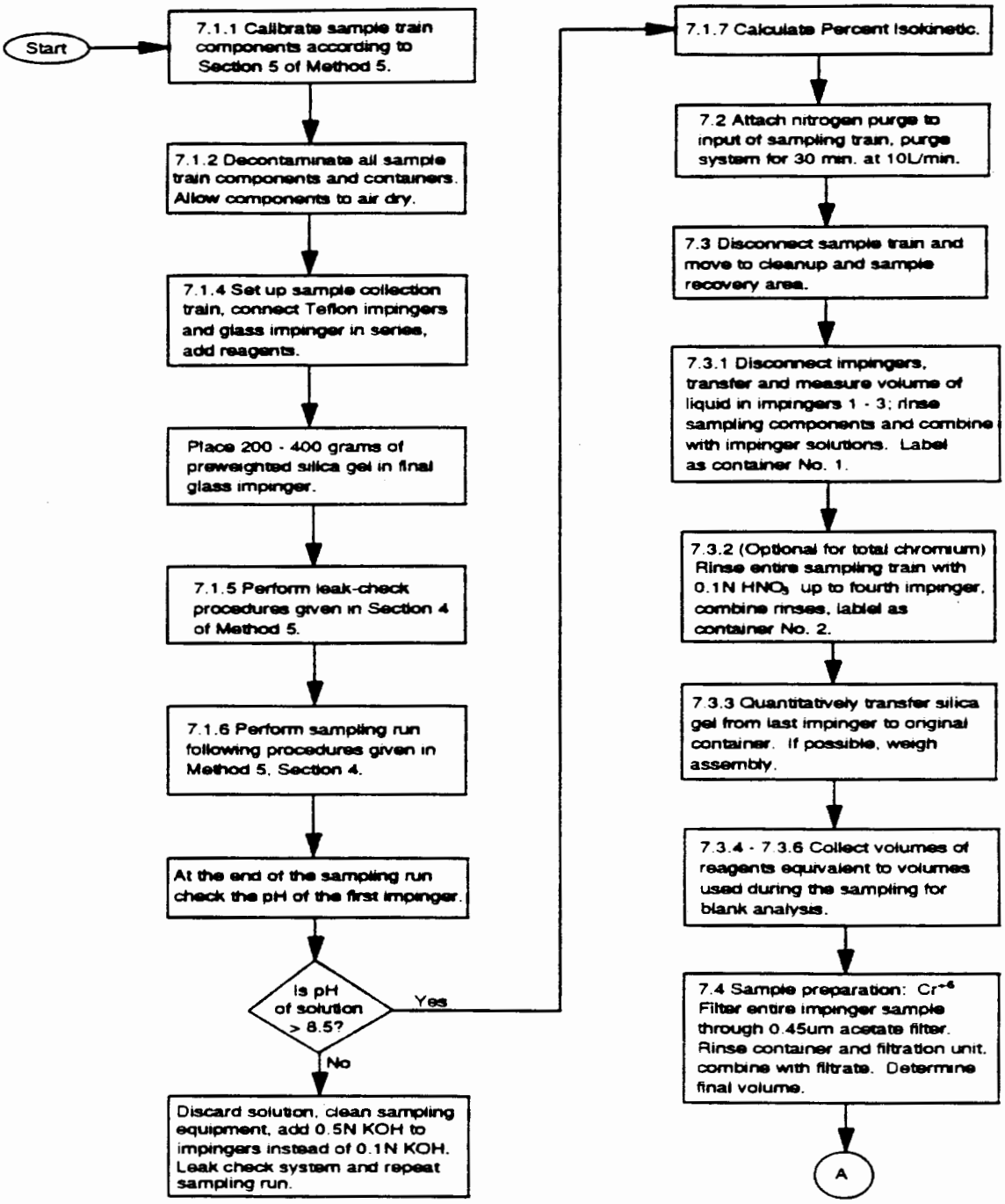
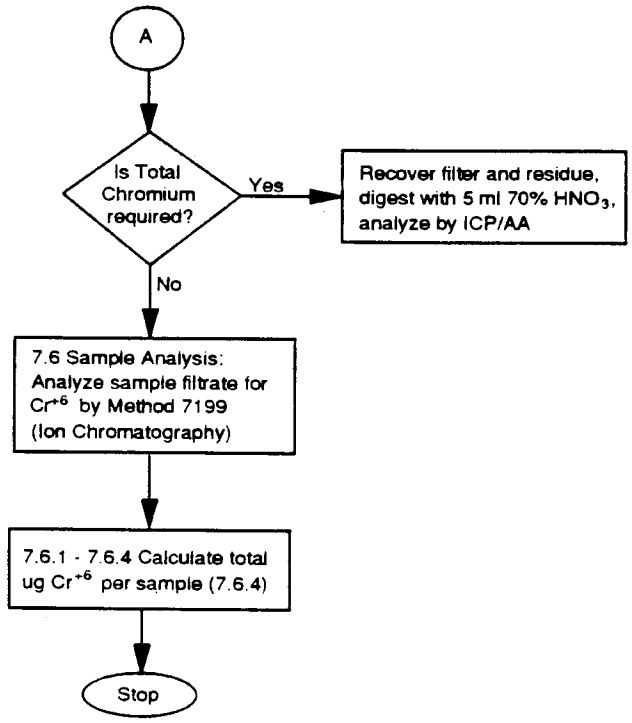


FIGURE 4. SCHEMATIC OF THE METHOD 0040 SAMPLING TRAIN

METHOD 0061
DETERMINATION OF HEXAVALENT CHROMIUM EMISSIONS
FROM STATIONARY SOURCES




A
Is Total Chromium required?
Yes
Recover filter and residue, digest with 5 ml 70% HNO_3, analyze by ICP/AA
No
7.6 Sample Analysis: Analyze sample filtrate for Cr^{+6} by Method 7199 (Ion Chromatography)
7.6.1 - 7.6.4 Calculate total ug Cr^{+6} per sample (7.6.4)
Stop

METHOD 0100

SAMPLING FOR FORMALDEHYDE AND OTHER CARBONYL COMPOUNDS IN INDOOR AIR

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the sampling of various carbonyl compounds in indoor air by derivatization with 2,4-dinitrophenylhydrazine (DNPH) in a silica gel cartridge. The method may be used in conjunction with Method 8315. The following compounds may be sampled by this method:

Compound Name	CAS No.[a]
Acetaldehyde	75-07-0
Acetone	67-64-1
Acrolein	107-02-8
Benzaldehyde	100-52-7
Butyraldehyde	123-72-8
Crotonaldehyde	123-73-9
2,5-Dimethylbenzaldehyde	5779-94-2
Formaldehyde	50-00-0
Hexanal	66-25-1
Isovaleraldehyde	590-86-3
Propionaldehyde	123-38-6
m-Tolualdehyde	620-23-5
o-Tolualdehyde	529-20-4
p-Tolualdehyde	104-87-0
Valeraldehyde	110-62-3

[a] Chemical Abstract Service Registry Number

1.2 This method is restricted to use by, or under the close supervision of, trained analytical personnel experienced in sampling organic compounds in air. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A known volume of indoor air is drawn through a prepacked silica gel cartridge coated with acidified 2,4-dinitrophenylhydrazine (DNPH), at a predetermined sampling rate for an appropriate period of time. After sampling, the sample cartridges are capped and placed in borosilicate glass tubes with polypropylene caps and placed in cold storage until analysis. The compounds of interest may then be eluted from the cartridge with acetonitrile from a plastic syringe reservoir into a graduated test tube or a volumetric flask. The eluate is then topped to known volume and refrigerated until analysis. Analysis may be done High Performance Liquid Chromatography (HPLC), Method 8315, with an ultraviolet (UV/Vis) detector at 360 nm.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware and other sample processing may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of analysis, by analyzing method blanks.

3.1.1 Glassware and plasticware must be scrupulously cleaned. Clean all glassware and plasticware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinsing with tap water, organic-free reagent water, and aldehyde-free acetonitrile. After cleaning, glassware and plasticware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.1.2 High purity reagents and solvents should be used to minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

3.1.3 Polyethylene gloves should be worn when handling the silica gel cartridges to reduce the possibility of contamination.

3.2 Contamination of the DNPH reagent is a frequently encountered problem. Formaldehyde, acetone, and 2,4-dinitroanaline (a decomposition product of DNPH) may be significant analytical impurities in the DNPH reagent at high concentrations. The DNPH must be purified by multiple recrystallizations in UV-grade acetonitrile. Recrystallization is accomplished, at 40-60°C, by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV-grade acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined prior to the analysis of the samples and should be less than 0.025 µg/mL. Refer to Sec. 5.9 for a recrystallization procedure.

3.3 Ozone Interferences - Ozone at high concentration has been shown to interfere negatively by reacting with both DNPH and its hydrazone derivatives in the cartridge (Ref. 6).

3.3.1 The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds during sampling. The presence of ozone in the sample stream is readily inferred from the appearance of new compounds with retention times shorter than that of the hydrazone of formaldehyde. Figure 1 shows chromatograms of samples of a formaldehyde-spiked air stream with and without ozone.

3.3.2 The most direct solution to the ozone interference is to remove the ozone before the sample stream reaches the cartridge. This process entails constructing an ozone denuder or scrubber and placing it on the front of the cartridge. The denuder is constructed out of 1 m of 0.64 cm OD copper tubing, which is filled with a saturated solution of KI water, allowed to stand for approximately 5 minutes, and dried with a stream of clean air or nitrogen for about 1 hour. The capacity of the ozone denuder as described is about 10,000 ppb/hour of ozone. Test aldehydes that were dynamically spiked into an ambient sample air stream passed through the denuder with virtually no losses.

3.4 Samples may be contaminated during shipment or storage by diffusion of volatile organics through the sample bottle septum seal. Field reagent blanks must be analyzed to determine when sampling and storage procedures have caused the contamination.

3.5 Matrix interferences may be caused by contaminants acquired by the sampling process. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. If significant interferences occur due to organic compounds that have the same retention time, altering the separation conditions by using alternative HPLC columns or mobile phase conditions may resolve the problem.

4.0 APPARATUS AND MATERIALS

4.1 Sampling Equipment

4.1.1 Sampling System - capable of accurately and precisely sampling 0.10 to 1.50 L/min of indoor air. The procedures given here assume use of a dry meter-equipped sampling system operated at flow rates of at least 0.5 L/min.

NOTE: A normal pressure drop through the sample cartridge approaches 19 kPa at a sampling rate of 1.5 L/min.

4.1.2 Thermometer and Barometer - to record indoor conditions at the time of sampling.

4.1.3 Stopwatch - to time sampling.

4.1.4 Rotameters - to allow observation of the flow rate without interruption of the sampling process.

4.1.5 Mass Flowmeters and Mass Flow Controllers - for metering and setting the air flow rate through the sample cartridge (0.50 to 1.20 L/min). These are necessary because cartridges have a high pressure drop and, at maximum flow rates, the cartridge behaves like a "critical orifice" and can display a flow rate drop over an extended sampling period (generally less than 5% over a 24 hour period).

4.1.6 Fittings and Plugs (Luer-Lok or equivalent) - to connect cartridges to the sampling system and to cap prepared cartridges.

4.1.7 Heated Probe - necessary when the temperature of sampled air is below 60°F, to insure effective collection of formaldehyde as a hydrazone.

4.1.8 Silica Gel Cartridges - chromatographic grade, 2 cm x 1.5 cm ID, with Luer-Lok type fittings on each end, for manual application of acidified DNPH coating (Sep-PAK from Waters Associates or equivalent). Commercially pre-packaged pre-coated cartridges are also available (Thermosorb/F cartridges from Thermedics Inc. and LpDNPH cartridges from Supelco, Inc. are examples).

4.2 Glassware

4.2.1 Volumetric Flasks - various sizes, 5 to 2000 mL.

4.2.2 Pipets - various sizes, 1 to 50 mL.

4.2.3 Sample Vials.

4.2.4 Borosilicate glass culture tubes (20 x 125 mm) with polypropylene screw caps - for transporting coated cartridges.

4.3 Liquid Syringes (polypropylene are adequate) - 10 mL, used to prepare DNPH-coated cartridges.

4.4 Syringe Rack - made of an aluminum plate with adjustable legs on all four corners. Circular holes of a diameter slightly larger than the diameter of the 10 mL syringes are drilled through the plate to allow batch processing of cartridges for cleaning, coating, and sample elution. A 0.16 x 36 x 53 cm plate with 45 holes in a 5x9 matrix is recommended. See Figure 2.

4.5 Cartridge Drying Manifold - has multiple standard male fittings (Luer-Lok or equivalent). See Figure 2.

4.6 Repetitive Dispensing Pipets - positive displacement, 0 to 10 mL range, with 1 L reagent bottles (Lab-Industries or equivalent).

4.7 Polyethylene Gloves - used to handle silica gel cartridges.

4.8 Sample Vial Holder - Friction-top metal can (e.g., 4 L paint can) or a styrofoam box lined with either polyethylene air bubble padding or granular charcoal to cushion the samples.

4.9 Soap Bubble Flowmeter or Calibrated Wet Test Meter - for calibrating the sampling flow rate.

4.10 Melting Point Apparatus (optional)

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Nitrogen gas, N_2 - high purity grade.

5.4 Acetonitrile, CH_3CN - UV grade.

5.5 Formaldehyde, CH_2O - ACS certified or assayed 36.5% solution (W/W).

5.6 Aldehydes and Ketones - analytical grade, used for preparation of DNPH derivative standards of target analytes other than formaldehyde. See list on page 1 for possible target analytes.

5.7 Perchloric Acid, $HClO_4$ - analytical grade.

CAUTION: Concentrated (69%) perchloric acid is a very strong oxidizing agent and presents a serious explosion hazard when combined with organic chemicals or materials. Any perchloric acid to be used in the preparation of DNPH, as per Sec. 5.9, must first be diluted with water to 3.8M as required in Sec. 5.9.5.

5.8 Hydrochloric Acid, HCl - analytical grade.

5.9 2,4-Dinitrophenylhydrazine (DNPH), $C_6H_6N_4O_4$ - recrystallize at least twice with UV grade acetonitrile using the following procedure:

NOTE: This procedure should be performed under a properly ventilated hood. Inhalation of acetonitrile can result in nose and throat irritation (brief exposure at 500 ppm) or more serious effects at higher concentration and/or longer exposures.

5.9.1 Prepare a saturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately 1 hour.

5.9.2 After 1 hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40 to 60°C. Maintain this temperature range until 95% of the solvent has evaporated leaving crystals.

5.9.3 Decant the solution to waste and rinse the remaining crystals twice with three times their apparent volume of acetonitrile.

5.9.4 Transfer the crystals to a clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let the crystals grow slowly at 40 to 60°C until 95% of the solvent has evaporated. Repeat the rinsing process as in Sec. 5.9.3.

5.9.5 Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 3.8 M perchloric acid per 100 mL of DNPH solution, and analyze by HPLC Method 8315). An acceptable impurity level is less than 0.025 mg/L of formaldehyde in recrystallized DNPH reagent or below the sensitivity (ppb, v/v) level indicated in Table 1 for the anticipated sample volume.

5.9.6 If the impurity concentration is not satisfactory, pipet off the solution to waste, repeat the recrystallization as in Sec. 5.9.4 but rinse with two 25 mL portions of acetonitrile. Prep and analyze the second rinse as in Sec. 5.9.5.

5.9.7 When the impurity concentration is satisfactory, place the crystals in an all-glass reagent bottle, add another 25 mL of acetonitrile, stopper, and shake the bottle. Use clean pipets when removing the saturated DNPH stock solution to reduce the possibility of contamination of the solution. Maintain only a minimum volume of the saturated solution adequate for day to day operation to minimize waste of the purified reagent.

5.10 Refer to the determinative method (Method 8315) for procedures regarding the preparation of DNPH derivatives, standards of the derivatives, and calibration standards for HPLC analysis. All standard solutions should be stored at about 4°C in a glass vial with a Teflon®-lined cap, with minimum headspace, and in the dark. They should be stable for about 6 weeks. All standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.11 Preparation of DNPH-Coated Sep-PAK Cartridges (if pre-packaged pre-coated cartridges, as in Sec. 4.1.8, are not used)

NOTE: This procedure must be performed in an atmosphere with a very low aldehyde background. The atmosphere above the acidified solution should preferably be filtered through a DNPH-coated silica gel cartridge to minimize contamination from laboratory air. All glassware and plasticware must be scrupulously cleaned and rinsed with deionized water and aldehyde free acetonitrile. Contact of reagents with laboratory air must be minimized. Polyethylene gloves must be worn when handling the cartridges.

5.11.1 DNPH Coating Solution

5.11.1.1 Pipet 30 mL of saturated DNPH stock solution into a 1000 mL volumetric flask, add 500 mL acetonitrile, and acidify with 1.0 mL of concentrated HCl.

5.11.1.2 Shake solution and dilute to volume with acetonitrile. Stopper the flask, invert, and shake several times until the solution is homogeneous. Transfer the acidified solution to a reagent bottle equipped with a 0 to 10 mL range repetitive pipet dispenser. Prime the dispenser and slowly dispense 10 to 20 mL to waste.

5.11.1.3 Dispense an aliquot solution to a sample vial, and check the impurity level of the acidified solution by HPLC according to Sec. 7.2.

5.11.1.4 The impurity concentration should be less than 0.025 µg/mL formaldehyde, similar to that in the DNPH stock solution.

5.11.2 Coating of Sep-PAK Cartridges

5.11.2.1 Open the Sep-PAK package, connect the short end to a 10 mL syringe and place it in the syringe rack. The syringe rack used for coating and drying the sample cartridges is illustrated in Figures 2(a) and 2(b).

5.11.2.2 Using a positive displacement, repetitive pipet, add 10 mL of acetonitrile to each of the syringes.

5.11.2.3 Let the liquid drain to waste by gravity. Remove any air bubbles that may be trapped between the syringe and the silica cartridge by displacing them with the acetonitrile in the syringe.

5.11.2.4 Once the effluent flow at the outlet of the cartridge has stopped, dispense 7 mL of the acidified DNPH coating reagent into each of the syringes using the repetitive pipet dispenser.

5.11.2.5 Let the coating reagent drain by gravity through the cartridge until flow at the other end of the cartridge stops.

5.11.2.6 Wipe the excess liquid at the outlet of each of the cartridges with clean tissue paper.

5.11.2.7 Assemble a drying manifold as shown in Figure 2(b). This contains a previously prepared, DNPH-coated, cartridge at each of the exit ports (e.g., these

scrubber or "guard cartridges" can be prepared by drying a few of the newly coated cartridges as per the following sections, and "sacrificing" these few to assure the purity of the rest). The "guard cartridges" serve to remove traces of formaldehyde that may be present in the nitrogen gas supply.

5.11.2.8 Insert cartridge connectors (flared at both ends, 0.64 cm OD x 2.5 cm Teflon® FEP tubing with ID slightly smaller than the OD of the cartridge port) onto the long end of the scrubber cartridges.

5.11.2.9 Remove the cartridges from the syringes and connect the short ends of the cartridges to the open end of the cartridge connectors already attached to the scrubber cartridges.

5.11.2.10 Pass nitrogen through each of the cartridges at about 300 to 400 mL/min.

5.11.2.11 Rinse the exterior surfaces and outlet end of the cartridges with acetonitrile using a Pasteur pipet.

5.11.2.12 After 15 minutes, stop the flow of nitrogen, wipe the cartridge exterior free of rinse acetonitrile and remove the dried cartridges.

5.11.2.13 Plug both ends of the coated cartridge with standard polypropylene Luer-Lok male plugs and place the plugged cartridge in a borosilicate glass culture tube with polypropylene screw caps.

5.11.2.14 Put a serial number and a lot number label on each of the individual cartridge glass storage containers and refrigerate the prepared lot until use. Cartridges will maintain their integrity for up to 90 days stored in refrigerated, capped culture tubes.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Assemble the sampling system, and ensure that the pump is capable of constant flow rate throughout the sampling period. The coated cartridges can be used as direct probes and traps for sampling indoor air when the temperature is above 60°F.

6.1.1 If the temperature in below 60°F, use the heated probe, mentioned in Sec. 4.1.7, to warm the air entering the sampling equipment.

6.1.2 If necessary, add an ozone denuder (see Sec. 3.3).

6.2 Before sample collection, check the system for leaks. Plug the input (short end) of the cartridge so no flow is indicated at the output end of the pump. The mass flowmeter should not indicate any air flow through the sampling apparatus.

6.3 Install the entire assembly (including a "dummy" sampling cartridge) and check the flow rate at a value near the desired rate. In general, flow rates of 500-1200 mL/min should be employed. The total moles of carbonyl in the volume of air sampled should not exceed that of the DNPH (2 mg or 0.01 mmole/cartridge). In general, a safe estimate of the sample size should be approximately 75% of the DNPH loading of the cartridge (approximately 200 µg as HCHO). Generally, calibration

is accomplished using a soap bubble flowmeter or calibrated wet test meter connected to the flow exit, assuming the system is sealed.

NOTE: ASTM Method D3686 describes an appropriate calibration scheme that does not require a sealed flow system downstream of the pump.

6.4 Ideally, a dry gas meter is included in the system to measure and record total flow. If a dry gas meter is not available, the operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. If the sampling period exceeds two hours, the flow rate should be measured at intermediate points during the sampling period. Include a rotameter to allow observation of the flow rate without interruption of the sampling process.

6.5 Before sampling, remove the glass culture tube from the friction-top metal can or styrofoam box. Let the cartridge warm to room temperature in the glass tube before connecting it to the sample train.

6.6 Using polyethylene gloves, remove the coated cartridge from the glass tube and connect it to the sampling system with a Luer adapter fitting. Seal the glass tube for later use, and connect the cartridge to the sampling train so that the short end becomes the sample inlet.

6.7 Turn the sampler on, record the start time, and adjust the flow to the desired rate. A typical flow rate through one cartridge is 1.0 L/min and 0.8 L/min for two cartridges in tandem.

6.8 Operate the sampler for the desired period, with periodic recording of the sampling variables such as sample flow rate, pressure, and temperature.

6.9 At the end of the sampling period, stop the flow and record the stop time. If a dry gas meter or equivalent is not used, the flow rate must be checked just before stopping the flow. The average sample flow rate may be calculated using the equation in Sec. 9.1.1. If the flow rate at the beginning and end of the sampling period differ by more than 15%, the sample should be marked as suspect.

6.10 Immediately after sampling, remove the cartridge (using polyethylene gloves) from the sampling system, cap with Luer end plugs, and place it back in the original labeled glass culture tube. Cap the culture tube, seal it with Teflon® tape, label the tube, and place it in a friction-top can containing 2-5 cm of granular charcoal or styrofoam box with appropriate padding. Refrigerate the culture tubes until analysis. The refrigeration period prior to analysis should not exceed 30 days.

NOTE: If samples are to be shipped to a central laboratory for analysis, the duration of the non-refrigerated period should be kept to a minimum, preferably less than two days.

6.11 Use the equations found in Secs. 9.1.2 and 9.1.3 to calculate the total volume of air sampled and the total volume of air sampled at standard conditions.

7.0 SAMPLE RECOVERY

7.1 The samples are returned to the laboratory in a friction-top can containing 2 to 5 cm of granular charcoal and stored in a refrigerator until analysis. Alternatively, the samples may also be

stored alone in their individual glass containers. The time between sampling and analysis should not exceed 30 days.

7.2 Refer to the determinative method (Method 8315) for procedures regarding desorption of the sample from the cartridge and HPLC analysis preparation.

8.0 CALIBRATIONS

8.1 Refer to Sec. 6.0 for requirements regarding the calibration of the sampling system flow rate and equipment for the determination of total flow.

8.2 Refer to the determinative method for procedures regarding calibration of the HPLC analysis system.

8.3 Barometer - Adjust the barometer initially and before each test series to agree within ±2.5 mm Hg (±0.1 in Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level). Note that adjustment for elevation differences between the weather station and the sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increase.

8.4 Thermometers

8.4.1 If a mercury-in-glass reference thermometer is to be used, it must conform to ATSM E-1 63C or 63F specifications.

8.4.2 If a thermocouple is to be used, it must be calibrated in the laboratory according to the manufacturer's specifications. The calibration should be done both with and without the use of any extension leads.

9.0 CALCULATIONS

9.1 Calculation of the total volume of air sampled at standard conditions.

9.1.1 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate, FR_{ave} in mL/minute, may be calculated using the following equation:

$$FR_{ave} = \frac{FR_1 + FR_2 + ... + FR_N}{N}$$

where:

$FR_1, FR_2, ..., FR_N$ = Flow rates determined at the beginning, end, and intermediate points during sampling

N = Number of flow rates averaged

9.1.2 The total volume of air sampled at the measured temperature and pressure, V_{Tot} in liters (L), may be calculated using the following equation:

$$V_{Tot} = \frac{(Time_2 - Time_1)(FR_{ave})}{1{,}000}$$

where:

$Time_2$ = Stop time (min)
$Time_1$ = Start time (min)
$(Time_2 - Time_1)$ = Total sampling time (min)
FR_{ave} = Average flow rate (mL/min)

9.1.3 The total volume of air sampled converted to standard conditions, V_{TotStd} in liter (L) at 25°C and 101.3 kPa, may be calculated using the following equation:

$$V_{TotStd} = V_{Tot} \times \frac{P_{ave}}{101.3\ kPa} \times \frac{298°C}{(273°C + T_{ave})}$$

where:

V_{Tot} = Total sample volume (L) at measured temperature and pressure
P_{ave} = Average indoor pressure (kPa)
T_{ave} = Average indoor temperature (°C)

10.0 DETERMINATION OF VOLUME TO BE SAMPLED

10.1 Refer to Table 1 for information regarding method "sensitivity" at various sampling volumes.

11.0 QUALITY CONTROL

11.1 Refer to Chapter One for quality control procedures.

11.2 Method Blanks - A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

11.3 Field Blanks - Field blanks must be submitted with the samples at each sampling site or 10% of the field samples, whichever is larger, should be shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the cartridge. It is desirable to analyze blank cartridges retained in the laboratory (method blanks) as well, to distinguish between possible field and laboratory contamination.

11.4 Blank and Matrix Spikes - A procedure for spiking air sampling cartridges is not yet established for this sampling technique. Refer to Appendix A for information regarding possible techniques for accomplishing sample spiking. Proper QC procedures require that a blank spike and matrix spike be processed for each batch of 10 samples or less. As the MDL becomes better established for this method, the representative spike concentration should be set at 10 times the MDL, for that matrix, to account for interferences.

12.0 METHOD PERFORMANCE

12.1 The method detection limit (MDL) is defined as the minimum concentration of the test compound that can be measured and reported with 99 percent confidence as being greater than zero. The MDL actually achieved in a given analysis will vary, as it is dependent on instrument sensitivity and matrix effects. The MDLs for the target analytes in the method have not yet been established.

12.2 Table 1 illustrates the sensitivity for the target analytes of interest found in ambient air that have been identified using two Zorbax ODS columns in series.

13.0 REFERENCES

1. Winberry, Jr., W.T., Murphy, N.T., and Riggin, R.M., Method TO-11, Compendium of Methods For the Determination of Toxic Organic Compounds in Ambient Air, EPA-600/6-89-017, U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1988.

2. Tejada, S.B., "Standard Operating Procedure for DNPH-coated Silica Cartridges For Sampling Carbonyl Compounds in Air and Analysis by High-performance Liquid Chromatography," Unpublished, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1986.

3. Tejada, S.B., "Evaluation of Silica Gel Cartridges Coated in situ with Acidified 2,4-Dinitrophenylhydrazine for Sampling Aldehydes and Ketones in Air," Intern. J. Environ. Anal. Chem., Vol. 26:167-185, 1986.

4. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - Ambient Air Specific Methods, EPA-600/4-77-027A, U.S. Environmental Protection Agency, Research Triangle Park, NC, July 1979.

5. Riggin, R.M., Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, EPA-600/4-83-027, U.S. Environmental Protection Agency, Research Triangle Park, NC, June, 1983.

6. Arnts, R.R. and Tejada, S.B., "2,4-Dinitrophenylhydrazine-Coated Silica Gel Cartridge Method for Determination of Formaldehyde in Air", Env. Sci. and Tech. 23, 1428-1430 (1989).

TABLE 1

SENSITIVITY (PPB, V/V) OF SAMPLING AND ANALYSIS FOR ALDEHYDES AND KETONES IN AMBIENT AIR USING AN ADSORBENT CARTRIDGE FOLLOWED BY GRADIENT HPLC[a]

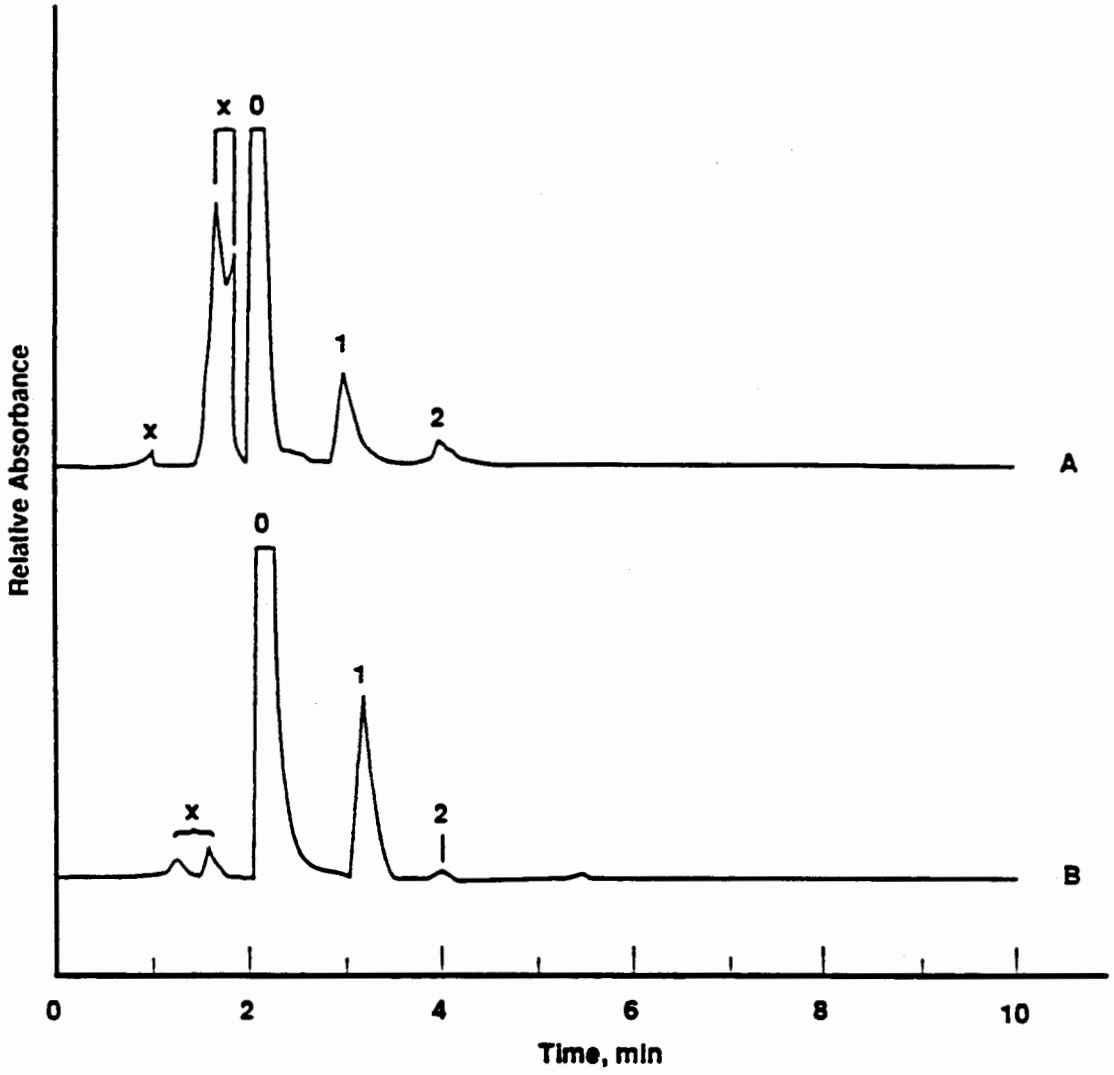
	Sample Volume (L)[b]									
Compound	10	20	30	40	50	100	200	300	400	500
Acetaldehyde	1.36	0.68	0.45	0.34	0.27	0.14	0.07	0.05	0.03	0.03
Acetone	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
Acrolein	1.29	0.65	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
Benzaldehyde	1.07	0.53	0.36	0.27	0.21	0.11	0.05	0.04	0.03	0.02
Butyraldehyde	1.21	0.61	0.40	0.30	0.24	0.12	0.06	0.04	0.03	0.02
Crotonaldehyde	1.22	0.61	0.41	0.31	0.24	0.12	0.06	0.04	0.03	0.02
2,5-Dimethyl-benzaldehyde	0.97	0.49	0.32	0.24	0.19	0.10	0.05	0.03	0.02	0.02
Formaldehyde	1.45	0.73	0.48	0.36	0.29	0.15	0.07	0.05	0.04	0.03
Hexanal	1.09	0.55	0.36	0.27	0.22	0.11	0.05	0.04	0.03	0.02
Isovaleraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02
Propionaldehyde	1.28	0.64	0.43	0.32	0.26	0.13	0.06	0.04	0.03	0.03
m-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
o-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
p-Tolualdehyde	1.02	0.51	0.34	0.25	0.20	0.10	0.05	0.03	0.03	0.02
Valeraldehyde	1.15	0.57	0.38	0.29	0.23	0.11	0.06	0.04	0.03	0.02

[a] The ppb values are measured at 1 atm and 25°C. The sample cartridge is eluted with 5 mL acetonitrile and 25 µL is injected into the HPLC. The maximum sampling flow through a DNPH-coated Sep-PAK is about 1.5 L/minute.

[b] A sample volume of 1000 L was also performed. The results show a sensitivity of 0.01 ppb for all the target analytes.

FIGURE 1

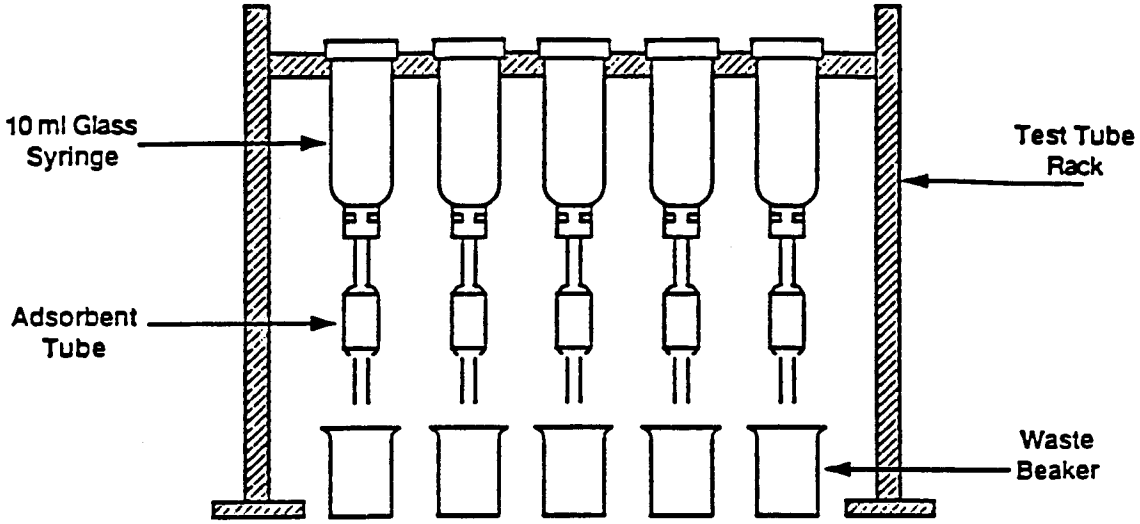
CARTRIDGE SAMPLES OF A FORMALDEHYDE AIR STREAM
WITH (A) AND WITHOUT (B) OZONE



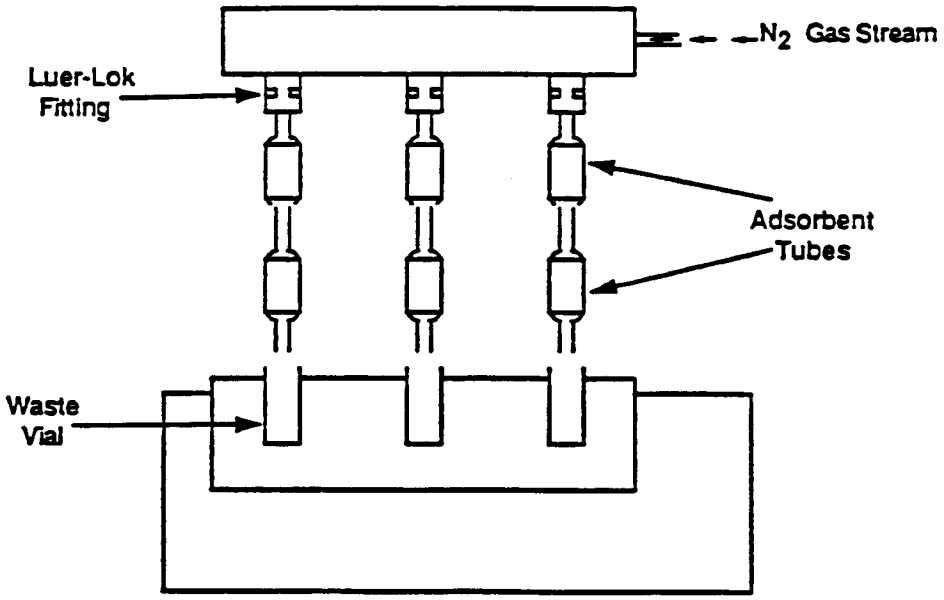
x = unknown
0 = DNPH
1 = formaldehyde
2 = acetaldehyde

FIGURE 2

SYRINGE RACKS FOR COATING AND DRYING SAMPLE CARTRIDGES



(a) RACK FOR COATING CARTRIDGES



(b) RACK FOR DRYING DNPH-COATED CARTRIDGES

This method does not contain a procedure for spiking cartridges for blank spikes and matrix spikes to determine percent recovery. Two suggested techniques for spiking cartridges are as follows:

1) A spike may be performed by introducing an aliquot of a solution containing the target analytes by pipet or syringe directly onto a cartridge in the field or in the laboratory. Standard spike and recovery procedures are followed and the field spike sample is returned to the laboratory for analysis. An aliquot of the field spike standard is retained in the laboratory for derivatization and comparative analysis.

2) Another technique would include spiking the sampling cartridge using a TGM 555 analyzer which produces gaseous formaldehyde standards. However, it should be noted that the procedures required to produce accurate, dynamic, low-level standard mixtures of organics in air are non-routine. The techniques developed for use in evaluating other air sampling procedures employ a 3-stage dynamic gas dilution system coupled with a constant-rate vapor generation assembly containing a trioxane permeation tube (VICI Medtronics Dynacal permeation device or equivalent) that is maintained at 55°C. Trioxane vapor is converted stoichiometrically to formaldehyde vapor using a special high-temperature (160°C) catalytic converter assembly. This method of sample introduction has been used when testing continuous sampling apparatus.

METHOD 1010
PENSKY-MARTENS CLOSED-CUP METHOD FOR DETERMINING IGNITABILITY

1.0 SCOPE AND APPLICATION

1.1 Method 1010 uses the Pensky-Martens closed-cup tester to determine the flash point of liquids including those that tend to form a surface film under test conditions. Liquids containing non-filterable, suspended solids shall also be tested using this method.

2.0 SUMMARY OF METHOD

2.1 The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

For further information on how to conduct a test by this method, see Reference 1 below.

3.0 METHOD PERFORMANCE

3.1 The Pensky-Martens and Setaflash Closed Testers were evaluated using five industrial waste mixtures and p-xylene. The results of this study are shown below in °F along with other data.

Sample	Pensky-Martens	Setaflash
1[2]	143.7 ± 1.5	139.3 ± 2.1
2[2]	144.7 ± 4.5	129.7 ± 0.6
3[2]	93.7 ± 1.5	97.7 ± 1.2
4[2]	198.0 ± 4.0	185.3 ± 0.6
5[2]	119.3 ± 3.1	122.7 ± 2.5
p-xylene[2]	81.3 ± 1.1	79.3 ± 0.6
p-xylene[3]	77.7 ± 0.5[a]	--
Tanker oil	125, 135	--
Tanker oil	180, 180	--
Tanker oil	110, 110	--
DIBK/xylene	102 ± 4[b]	107

[b]75/25 v/v analyzed by four laboratories.
[a]12 determinations over five-day period.

4.0 REFERENCES

1. D 93-80, Test Methods for Flash Point by Pensky-Martens Closed Tester, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, 04.09, 1986.

2. Umana, M., Gutknecht, W., Salmons, C., et al., Evaluation of Ignitability Methods (Liquids), EPA/600/S4-85/053, 1985.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

METHOD 1020A

SETAFLASH CLOSED-CUP METHOD FOR DETERMINING IGNITABILITY

1.0 SCOPE AND APPLICATION

1.1 Method 1020 makes use of the Setaflash Closed Tester to determine the flash point of liquids that have flash points between 0° and 110°C (32° and 230°F) and viscosities lower than 150 stokes at 25°C (77°F).

1.2 The procedure may be used to determine whether a material will or will not flash at a specified temperature or to determine the finite temperature at which a material will flash.

1.3 Liquids that tend to form surface films under test conditions or those that contain non-filterable suspended solids shall be tested for ignitability using Method 1010 (Pensky-Martens Closed-Cup).

2.0 SUMMARY OF METHOD

2.1 By means of a syringe, 2-mL of sample is introduced through a leak-proof entry port into the tightly closed Setaflash Tester or directly into the cup which has been brought to within 3°C (5°F) below the expected flash point.

2.2 As a flash/no-flash test, the expected flash-point temperature may be a specification (e.g., 60°C). For specification testing, the temperature of the apparatus is raised to the precise temperature of the specification flash point by slight adjustment of the temperature dial. After 1 minute, a test flame is applied inside the cup and note is taken as to whether the test sample flashes or not. If a repeat test is necessary, a fresh sample should be used.

2.3 For a finite flash management, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5°C (9°F) intervals until a flash is observed. A repeat determination is then made using a fresh sample, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 0.5°C (1°F) intervals.

For further information on how to conduct a test with this method, see Reference 1 below.

3.0 METHOD PERFORMANCE

See Method 1010.

4.0 REFERENCES

1. D-3278-78, Test Method for Flash Point of Liquids by Setaflash Closed Tester, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

2. Umana, M., Gutknecht, W., Salmons, C., et al., Evaluation of Ignitability Methods (Liquids), EPA/600/S4-85/053, 1985.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

METHOD 1030

IGNITABILITY OF SOLIDS

1.0 SCOPE AND APPLICATION

1.1 This method is suitable for the determination of the ignitability of solids and is appropriate for pastes, granular materials, solids that can be cut into strips, and powdery substances. This method may be used to meet certain regulatory applications; with respect to the characteristic of ignitability in CFR § 261.21, this method may be used, but is not required, to determine whether a solid waste "when ignited, burns so vigorously and persistently that it creates a hazard." If it is impractical to perform the test because of the physical form of the sample, generator knowledge should be used to determine the ignitability hazard posed by the material.

2.0 SUMMARY OF METHOD

2.1 In a preliminary test, the test material is formed into an unbroken strip or powder train 250 mm in length. An ignition source is applied to one end of the test material to determine whether combustion will propagate along 200 mm of the strip within a specified time period. Materials that propagate burning along a 200 mm strip within the specified time period are then subjected to a burning rate test. Materials that do not ignite or propagate combustion as described above do not require further testing. In the burning rate test, the burning time is measured over a distance of 100 mm and the rate of burning is determined. The test method described here is based on the test procedure adopted by the Department of Transportation from the United Nations regulations for the international transportation of dangerous goods and is contained in Appendix E to Part 173 of 49 CFR.

3.0 INTERFERENCES

3.1 In laboratory tests the burning rate of duplicate runs is usually repeatable to within 10%. However, large differences in burning rates may occur if experimental conditions are not held constant. Variation in airflow rates, particle size, and moisture content of the test material will affect test results. Therefore, at least triplicate determinations of the burning rate should be conducted.

3.2 Particle size of test material can affect not only the burning rate, but also the ignition of the material. Therefore, the particle size of the test material should be the same for each test run. The particle size of the test material should be reported in a simple descriptive format (e.g., fine powder, sand, coarse granular).

3.3 Temperature of some test material such as sulfur powder affects the burning rate. For reproducible results, all tests should be performed at approximately the same initial temperature (ambient room or laboratory temperature).

3.4 All tests must be carried out inside a fume hood with the test apparatus situated perpendicular (90^{o}) to the direction of airflow. Airflow parallel (0^{o}) to the test apparatus results in non-reproducible burning rates.

3.5 The rate of airflow through the fume hood affects the burning rate. Too high an airflow distorts the flame and retards its horizontal propagation. The optimum airflow appears to be in the range of 0.7-1 meter per second.

3.6 Materials that are moisture sensitive (i.e., readily absorb moisture from air) should be tested as quickly as possible after removal from the sample container. All materials should be tested as received by the laboratory.

4.0 APPARATUS AND MATERIALS

4.1 Low-heat conducting, non-combustible, impervious ceramic tile or equivalent material, of approximate dimension of 25 cm x 25 cm x 2.5 cm (the tile must be at least 25 cm in length to support a 250 mm test sample).

4.2 High temperature marker or equivalent marking device for marking ceramic plates.

4.3 Powder Train Mold (see Figure 1) for molding powdered and granular materials for the burn rate test. The material of construction can be aluminum, brass, stainless steel, or plastic. The mold is 250 mm in length and has a triangular cross-section, with a width of 20 mm, and a depth of 10 mm as measured from the bottom of the triangular opening to where the sides meet. On both sides of the mold, in the longitudinal direction, two sheets are mounted as lateral limitations which extend 2 mm beyond the upper edge of the triangular cross-section. This device can be fabricated by most machine shops. The complete burn rate apparatus is available from: Associated Design and Manufacturing Co.; 814 N. Henry Street; Alexandria, Virginia 22314.

4.4 A Bunsen (propane gas and air) burner with a minimum diameter of 5 mm capable of attaining a temperature of at least 1,000^{o}C.

4.5 Stop watch.

4.6 Thermocouple to measure the temperature of the gas flame.

4.7 Thermometer to measure initial temperature of material (i.e., room temperature).

4.8 Anemometer to measure airflow in the fume hood.

5.0 REAGENTS

5.1 No special reagents are required to conduct this test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples are tested on as-received basis unless requested otherwise. No sample preservation is required, but sample containers should be completely filled and tightly sealed to preserve sample integrity.

6.2 Samples should be tested as soon as possible after removal from the sample container (i.e., samples should not be allowed to dry or absorb moisture for excessive periods or to

lose volatiles). Samples that are chilled or cooled upon receipt to the laboratory should be allowed to equilibrate to the ambient laboratory temperature in the sample container.

7.0 PROCEDURE

SAFETY: Prior to starting the preliminary test, all sample materials must be tested to determine if that material is explosive or extremely flammable. Use a very small portion of material (1 gram or less). If the sample displays explosivity or extreme flammability, do not conduct this test.

7.1 Preliminary Screening Test

7.1.1 The preliminary ignitability test is conducted on all waste materials. On a clean, impervious ceramic tile (Section 4.1), clearly mark a 250 mm long test path. Make another mark at exactly 200 mm from the start of the sample path.

7.1.2 Prepare the test material in its "as received" form by forming an unbroken strip or powder train of sample 250 mm long by 20 mm wide by 10 mm high on the ceramic tile. Use the mold to form the material as in 7.2.3 if appropriate.

7.1.3 Place the ceramic tile with the loaded sample in a fume hood about 20 cm (~8 inches) from the front of the hood and in an area of laminar airflow. Position the sample perpendicular to the airflow. (See Figure 2) The airflow across the perpendicular axis of the sample should sufficient to prevent fumes from escaping into the laboratory and should not be varied during the test. The air velocity should be approximately 0.7 meters/second. Measure the air velocity by an anemometer.

7.1.4 Light the Bunsen burner and adjust the height of the flame (6.5 to 7.5 cm) by adjusting the propane gas and air flows. Measure the temperature of the flame (tip of the flame) by a thermocouple. The temperature of the flame must be at least 1000°C.

7.1.5 Apply the tip of the flame to one end of the sample strip . The test period will depend on the sample matrix as follows:

7.1.6 If the waste is non-metallic, hold the flame tip on the sample strip until the sample ignites or for a maximum of 2 minutes. If combustion occurs, begin timing with a stop watch and note whether the combustion propagates up to the 200 mm mark within the 2 minute test period.

7.1.7 If the waste is a metal or metal-alloy powder, hold the flame tip on the sample strip until the sample ignites or for a maximum of 5 minutes. If combustion occurs, begin timing with a stop watch and note whether the combustion propagates up to the 200 mm mark within the 20 minute test period.

7.1.8 If the waste does not ignite and propagate combustion either by burning with open flame or by smoldering along 200 mm of sample strip within the 2 minute test period (or 20 minute test period for metal powders), the waste is not considered flammable and no further testing is required. If the waste propagates burning of 200 mm of the test strip within

the 2 minute test period (20 minute test period for metals), the material must be evaluated by the burning rate test (Section 7.2).

7.2 Burning Rate Test

7.2.1 The preparation of the test sample for the burning rate test will depend on the physical characteristics of the waste. Wastes that exist in a powdered or granular state are molded in a powder train mold shown in Figure 1. Pasty materials are formed into a rope 250 mm in length with a cross-section of 1 cm^2. All tests for the burn rate test are performed on clean, ambient temperature, ceramic plates.

7.2.2 On a clean, impervious ceramic tile (Section 4.1), clearly mark a 250 mm long test path. Make two additional timing marks at 80 mm and 180 mm from the start of the sample path. The distance between the two marks (100 mm) will be used to calculate the rate of burn in Section 7.2.9.

7.2.3 Tighten the side plates on the mold. For powdered or granular materials: Place the mold on the base plate. Pour the material to fill the triangular cross section of the mold loosely.

7.2.4 Drop the unit from a height of 2 cm onto a solid surface three times to settle the powder. Remove the side supports. Lift the mold off the base plate. Place a clean ceramic test plate with the appropriate timing marks (Section 7.2.2) face down on top of the mold. Invert the setup and remove the mold.

7.2.5 Pasty wastes are prepared by spreading the waste on a marked ceramic tile (Section 7.2.2) in the form of a rope 250 mm in length with a cross-section of 1 cm^2.

7.2.6 Place the ceramic tile with the loaded sample prepared in Sections 7.2.3 or 7.2.5 in a fume hood about 20 cm (~8 inches) from the front of the hood and in an area of laminar airflow. Position the sample perpendicular to the airflow. (See Figure 2) The airflow across the perpendicular axis of the sample should sufficient to prevent fumes from escaping into the laboratory and should not be varied during the test. The air velocity should be approximately 0.7 meters/second. Measure the air velocity with an anemometer.

7.2.7 Light the Bunsen burner and adjust the height of the flame (6.5 to 7.5 cm) by adjusting the propane gas and air flows. Measure the temperature of the flame (tip of the flame) by a thermocouple. The temperature of the flame must be at least 1000°C.

7.2.8 Apply the tip of the flame to one end of the sample strip to ignite the test strip as described in Section 7.1.6 and 7.1.7.

7.2.9 When the test strip or powder train has burned up to the 80 mm time marker, begin timing the rate of combustion with a stop watch. Stop the timer when the burned strip reaches the 180 mm time marker. Record the amount of time (in seconds) required to burn the 100 mm test strip. Calculate the rate of burning by dividing the length of the burn test strip (100 mm) by the total time (seconds). Results of the burn rate test should be reported in mm/sec. Wastes that have a rate of burning of more than 2.2 mm/sec (or burn time of less than 45 seconds for 100 mm) are considered to have a positive result for ignitability

according to DOT regulations. For metals, this time is 10 minutes or less for 100 mm (or a burn rate of more than 0.17 mm/sec).

7.2.10 Report and Calculation Section

Test Material Information

Source of Material: e.g., Company, operation or process
Description of material: e.g., powder or paste, metallic or non-metallic
Particle size: e.g., fine powder, granular, sand, etc.
Preliminary Burning Time: ____ seconds.

Test Conditions

Date of Test:
Temperature of test material (°C):
Air velocity through fume hood (m/s):

Ignitability Test Data				
Test Number	Time (sec) elapsed between application of flame and start of ignition	Burning time over 100 mm (sec)	Burning Rate (mm/sec)	Comments
1				
2				
3				

8.0 QUALITY CONTROL

8.1 All tests must be performed on a clean ceramic plate at room temperature. All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

8.2 All replicate runs must be at the same initial temperature (ambient laboratory temperature).

8.3 All replicate tests must be run at approximately the same airflow through the fume hood.

8.4 Only materials of the same particle size distribution should be used for all replicate tests.

8.5 The burn rate test must be conducted in triplicate if the preliminary screening test is positive. Any burn rate for non-metallic samples that exceeds 2.2 mm/sec (or a burn time of less than 45 seconds for 100 mm) is considered to have a positive result. For metals, a burn rate of more than 0.17 mm/sec (or burn time of less than 10 minutes for 100 mm) is considered to have a positive result.

9.0 METHOD PERFORMANCE

9.1 An independent laboratory validation was conducted on the robustness of the burn rate test procedure. The materials selected for this evaluation included:

1. A 50/50 mixture of metallic silicon and lead dioxide ($Pb0_2$)
2. Excelsior
3. Dextrin (yellow powder)
4. Sulfur (fine yellow powder)
5. Aluminum metal (coarse)
6. Magnesium metal (coarse)
7. Polyethylene high density (granular)
8. Polyethylene low density (fluffy white powder)
9. Scott fertilizer (32-3-10:N-P-K)
10. JP-4 contaminated soil (approximately 5000 ppm)

Of these materials, the 50/50 mixture of metallic silicon and lead dioxide ($Pb0_2$), elemental sulfur, and excelsior were considered to give a positive ignitability result under the conditions of the test. The remaining materials gave negative (nonflammable) results under the conditions of the test. Several test variables including ignition source, ambient temperature, and apparatus orientation, were studied using these materials. Partial results of this study are summarized in Table 1.

9.2 In another evaluation of the DOT burn rate test, potentially ignitable finishing wastes from the furniture industry were collected and tested for burning rates. Each waste was tested in triplicate to establish a mean value for the burning rate. The results for the flammable wastes are summarized in Table 2.

9.3 In order to evaluate the ruggedness of the DOT burn rate test, select ignitable finishing wastes were split and tested by a state laboratory and an independent contract laboratory. The results of this comparison are summarized in Table 3.

10.0 REFERENCES

1. "Test Methods for Readily Combustible Solids. Burning Rate Test." (14.2.2.5). Recommendations on the Transport of Dangerous Goods. Fifth Revised Edition. United Nations, New York. 1988.

2. DOT Regulation. Appendix E to Part 173 of 49 CFR, Chapter 1 (12-31-91 Edition). pp. 597-598.

3. Flammability (solids). Method A.10. Official Journal of the European Communities. 9/19/84. No. L251/63.

4. "Validation of Ignitability Method For Solids" Foster Wheeler Enviresponse, Inc., Edison NJ., Submitted to the Office of Solid Waste, US EPA, February 1994.

5. Internal Report, (AMFA Report) North Carolina Department of Environmental Health and Natural Resources. (Bill Hamner)

TABLE 1
TEST VARIABLES FOR IGNITABILITY

Material Tested	Test Number	Variable combination[1]	Burn Time over 100 mm (sec)	Burn Rate (mm/sec)
50% Metallic Silicon and 50% Lead IV Oxide	1	ABC	0.84	119
	2	Abc	0.50	200
	3	aBc	0.69	145
	4	abC	0.65	154
Excelsior (wood shavings)	1	ABC	13.45	7.43
	2	Abc	9.14	10.9
	3	aBc	13.37	7.47
	4	abC	13.59	7.36

[1]where:

A-flame ignition
a-hot wire ignition source
B-ambient temperature of 20°C
b-ambient temperature of 100°C
C-orientation of test apparatus of 90° to air flow
c-orientation of test apparatus of 0° to air flow

TABLE 2
BURNING RATES FOR IGNITABLE WASTES

Sample No.	Description of Waste	Burn Time over 100 mm (sec)	Burn Rate (mm/sec)
A2	Segregated Lacquer Dust	4.7	21.3
J2	Segregated Lacquer Dust	4.6	21.7
U	Segregated Lacquer Dust	8.6	11.6
K	Consolidated Lacquer Dust	6.0	16.7
H	Catalyzed Lacquer Dust	6.7	14.9
F	Water Based Lacquer Dust	19.4	5.15
P	Booth Coat-Stain Overspray	12.5	8.0
O	Pallet Covered Cardboard	11.1	9.0
Q	Pallet Covered Cardboard	12.3	8.13

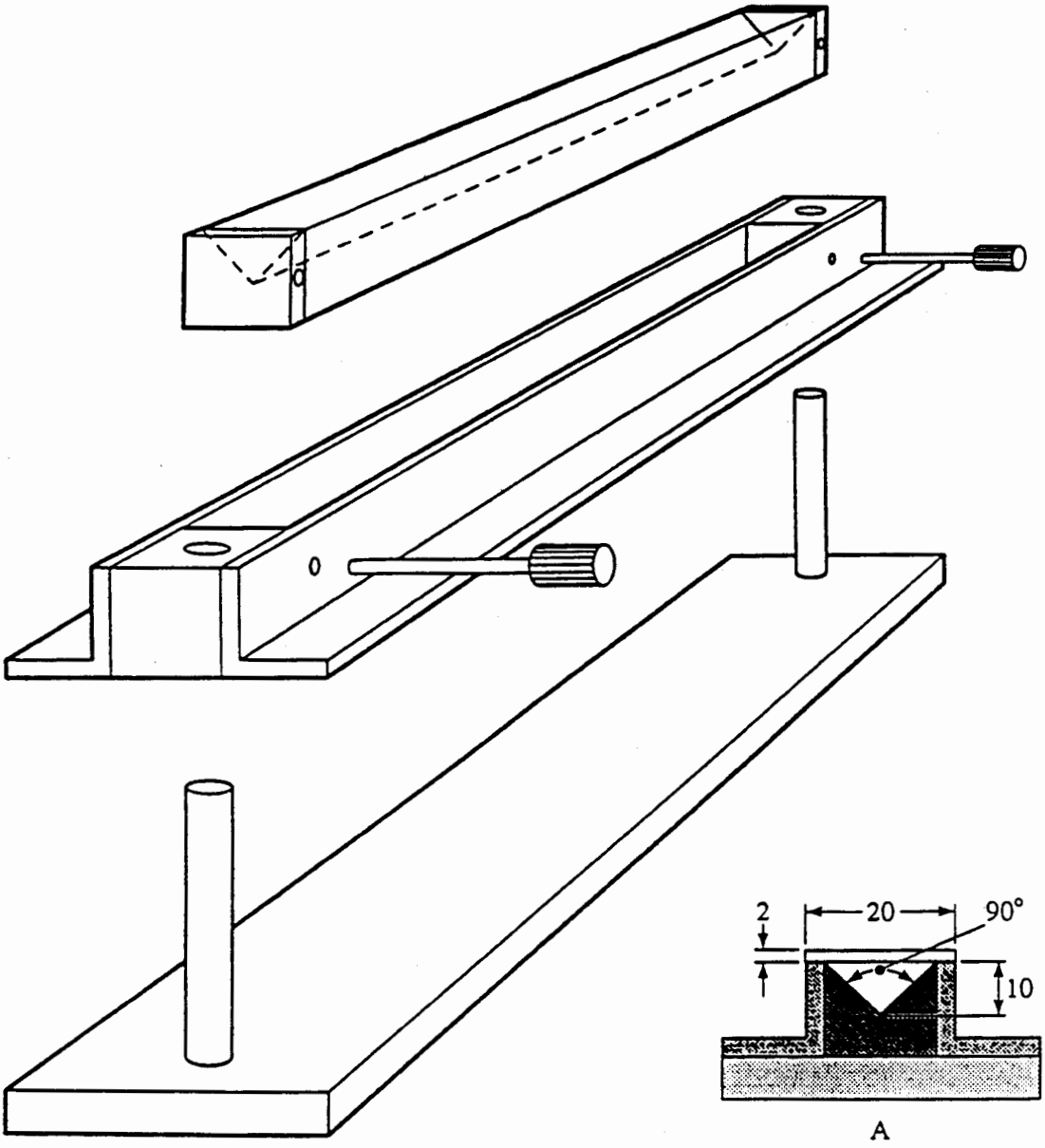
TABLE 3
COMPARISON OF BURN RATES

Sample No.	Description of Waste	Mean Burn Time Over 100 mm in Seconds	
		State Laboratory	Contract Laboratory
A1	Segregated Lacquer Dust	4.7	5
J1	Segregated Lacquer Dust	4.6	4.3
12	Booth Coat-Glaze Overspray	0[1]	0[1]

[1] Waste was found to be nonflammable under conditions of the test.

Figure 1

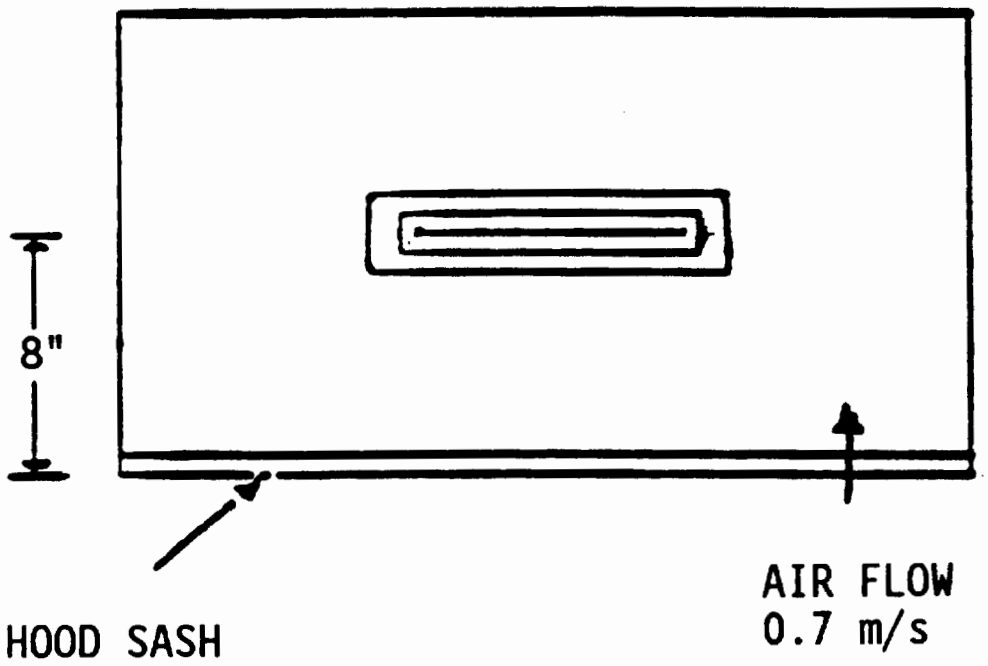
Powder Train Mold

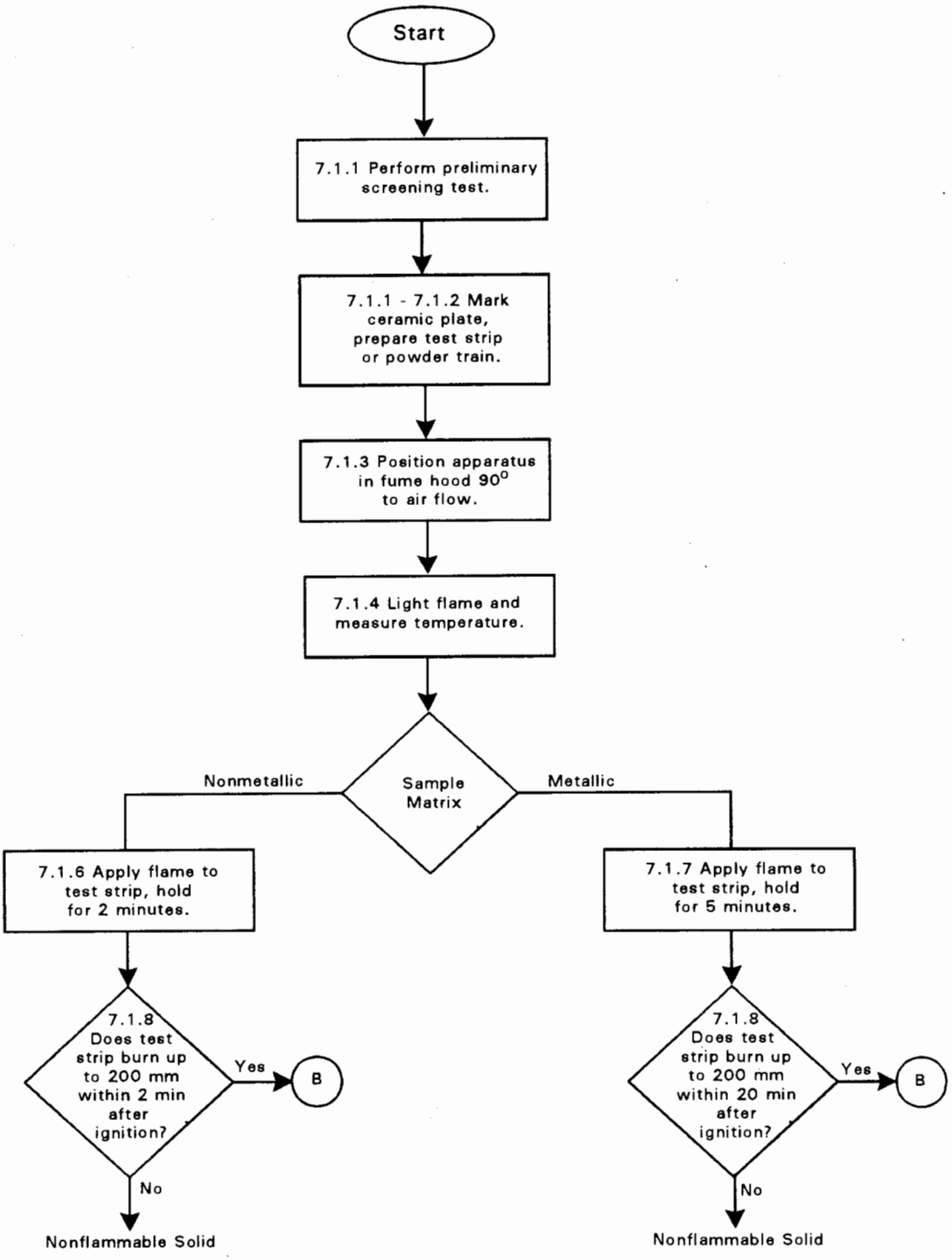


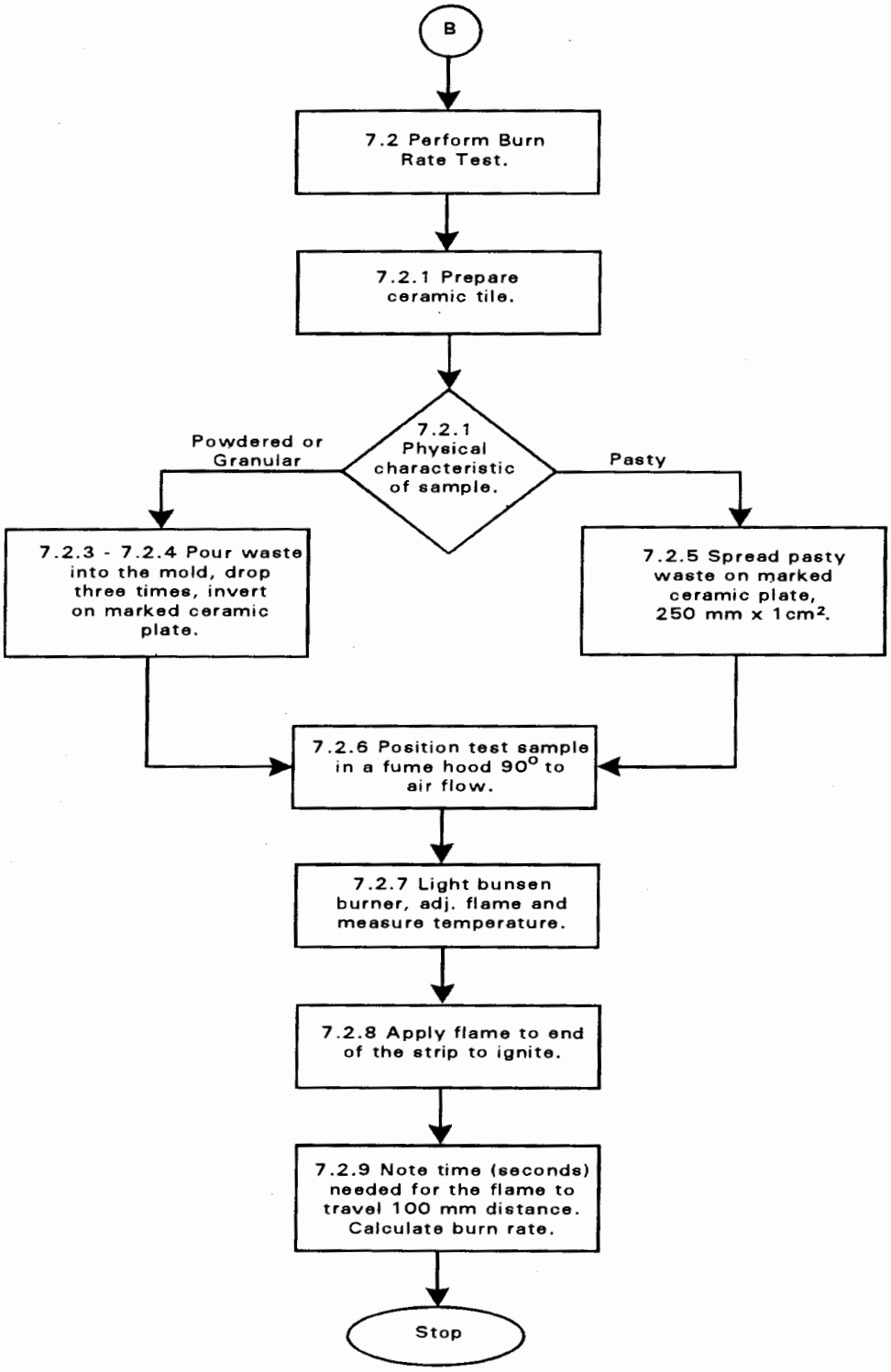
(A) Cross-section of 250 mm long mould

Figure 2

Test Apparatus Position in Fume Hood




Start
7.1.1 Perform preliminary screening test.
7.1.1 - 7.1.2 Mark ceramic plate, prepare test strip or powder train.
7.1.3 Position apparatus in fume hood 90° to air flow.
7.1.4 Light flame and measure temperature.
Sample Matrix
Nonmetallic
Metallic
7.1.6 Apply flame to test strip, hold for 2 minutes.
7.1.7 Apply flame to test strip, hold for 5 minutes.
7.1.8 Does test strip burn up to 200 mm within 2 min after ignition?
Yes
B
No
Nonflammable Solid
7.1.8 Does test strip burn up to 200 mm within 20 min after ignition?
Yes
B
No
Nonflammable Solid


B
7.2 Perform Burn Rate Test.
7.2.1 Prepare ceramic tile.
7.2.1 Physical characteristic of sample.
Powdered or Granular
Pasty
7.2.3 - 7.2.4 Pour waste into the mold, drop three times, invert on marked ceramic plate.
7.2.5 Spread pasty waste on marked ceramic plate, 250 mm x 1cm².
7.2.6 Position test sample in a fume hood 90° to air flow.
7.2.7 Light bunsen burner, adj. flame and measure temperature.
7.2.8 Apply flame to end of the strip to ignite.
7.2.9 Note time (seconds) needed for the flame to travel 100 mm distance. Calculate burn rate.
Stop

METHOD 1110

CORROSIVITY TOWARD STEEL

1.0 SCOPE AND APPLICATION

1.1 Method 1110 is used to measure the corrosivity toward steel of both aqueous and nonaqueous liquid wastes.

2.0 SUMMARY OF METHOD

2.1 This test exposes coupons of SAE Type 1020 steel to the liquid waste to be evaluated and, by measuring the degree to which the coupon has been dissolved, determines the corrosivity of the waste.

3.0 INTERFERENCES

3.1 In laboratory tests, such as this one, corrosion of duplicate coupons is usually reproducible to within 10%. However, large differences in corrosion rates may occasionally occur under conditions where the metal surfaces become passivated. Therefore, at least duplicate determinations of corrosion rate should be made.

4.0 APPARATUS AND MATERIALS

4.1 An apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5,000 mL), a reflux condenser, a thermowell and temperature regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. A typical resin flask set up for this type of test is shown in Figure 1.

4.2 The supporting device and container shall be constructed of materials that are not affected by, or cause contamination of, the waste under test.

4.3 The method of supporting the coupons will vary with the apparatus used for conducting the test, but it should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include glass, fluorocarbon, or coated metal.

4.4 The shape and form of the coupon support should ensure free contact with the waste.

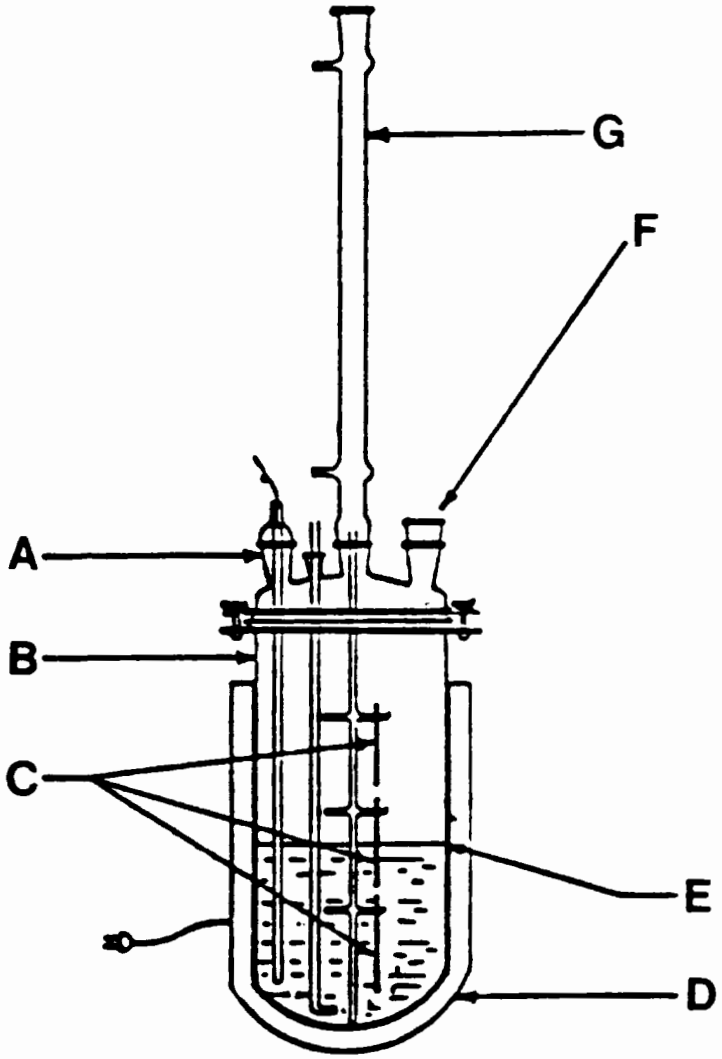


Figure 1. Typical resin flask that can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of the flask top is such that more sophisticated apparatus can be added as required by the specific test being conducted. A = thermowell, B = resin flask, C = specimens hung on supporting device, D = heating mantle, E = liquid interface, F = opening in flask for additional apparatus that may be required, and G = reflux condenser.

4.5 A circular specimen of SAE 1020 steel of about 3.75 cm (1.5 in.) diameter is a convenient shape for a coupon. With a thickness of approximately 0.32 cm (0.125 in.) and a 0.80-cm (0.4-in.)-diameter hole for mounting, these specimens will readily pass through a 45/50 ground-glass joint of a distillation kettle. The total surface area of a circular specimen is given by the following equation:

$$A = 3.14/2(D^2-d^2) + (t)(3.14)(D) + (t)(3.14)(d)$$

where:

t = thickness.
D = diameter of the specimen.
d = diameter of the mounting hole.

If the hole is completely covered by the mounting support, the last term in the equation, (t)(3.14)(d), is omitted.

4.5.1 All coupons should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to ±1% is usually adequate.

4.5.2 More uniform results may be expected if a substantial layer of metal is removed from the coupons prior to testing the corrosivity of the waste. This can be accomplished by chemical treatment (pickling), by electrolytic removal, or by grinding with a coarse abrasive. At least 0.254 mm (0.0001 in.) or 2-3 mg/cm^2 should be removed. Final surface treatment should include finishing with #120 abrasive paper or cloth. Final cleaning consists of scrubbing with bleach-free scouring powder, followed by rinsing in distilled water and then in acetone or methanol, and finally by air-drying. After final cleaning, the coupon should be stored in a desiccator until used.

4.5.3 The minimum ratio of volume of waste to area of the metal coupon to be used in this test is 40 mL/cm^2.

5.0 REAGENTS

5.1 Sodium hydroxide (NaOH), (20%): Dissolves 200 g NaOH in 800 mL Type II water and mix well.

5.2 Zinc dust.

5.3 Hydrochloric acid (HCl): Concentrated.

5.4 Stannous chloride ($SnCl_2$).

5.5 Antimony chloride ($SbCl_3$).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 Assemble the test apparatus as described in Paragraph 4.0, above.

7.2 Fill the container with the appropriate amount of waste.

7.3 Begin agitation at a rate sufficient to ensure that the liquid is kept well mixed and homogeneous.

7.4 Using the heating device, bring the temperature of the waste to 55°C (130°F).

7.5 An accurate rate of corrosion is not required; only a determination as to whether the rate of corrosion is less than or greater than 6.35 mm per year is required. A 24-hr test period should be ample to determine whether or not the rate of corrosion is >6.35 mm per year.

7.6 In order to determine accurately the amount of material lost to corrosion, the coupons have to be cleaned after immersion and prior to weighing. The cleaning procedure should remove all products of corrosion while removing a minimum of sound metal. Cleaning methods can be divided into three general categories: mechanical, chemical, and electrolytic.

7.6.1 Mechanical cleaning includes scrubbing, scraping, brushing, and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods. The others are used in cases of heavy corrosion as a first step in removing heavily encrusted corrosion products prior to scrubbing. Care should be taken to avoid removing sound metal.

7.6.2 Chemical cleaning implies the removal of material from the surface of the coupon by dissolution in an appropriate solvent. Solvents such as acetone, dichloromethane, and alcohol are used to remove oil, grease, or resinous materials and are used prior to immersion to remove the products of corrosion. Solutions suitable for removing corrosion from the steel coupon are:

Solution	Soaking Time	Temperature
20% NaOH + 200 g/L zinc dust	5 min	Boiling
or		
Conc. HCl + 50 g/L $SnCl_2$ + 20 g/L $SbCl_3$	Until clean	Cold

7.6.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed uses:

Solution:	50 g/L H_2SO_4
Anode:	Carbon or lead
Cathode:	Steel coupon
Cathode current density:	20 amp/cm^2 (129 amp/$in.^2$)
Inhibitor:	2 cc organic inhibitor/liter
Temperature:	74°C (165°F)
Exposure Period:	3 min.

NOTE: Precautions must be taken to ensure good electrical contact with the coupon to avoid contamination of the cleaning solution with easily reducible metal ions and to ensure that inhibitor decomposition has not occurred. Instead of a proprietary inhibitor, 0.5 g/L of either diorthotolyl thiourea or quinolin ethiodide can be used.

7.7 Whatever treatment is employed to clean the coupons, its effect in removing sound metal should be determined by using a blank (i.e., a coupon that has not been exposed to the waste). The blank should be cleaned along with the test coupon and its waste loss subtracted from that calculated for the test coupons.

7.8 After corroded specimens have been cleaned and dried, they are reweighed. The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. In order to determine the corrosion rate for the purpose of this regulation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{\text{weight loss x } 11.145}{\text{area x time}}$$

where: weight loss is in milligrams,
area in square centimeters,
time in hours, and
corrosion rate in millimeters per year (mmpy).

8.0 QUALITY CONTROL

8.1 All quality control data should be filed and available for auditing.

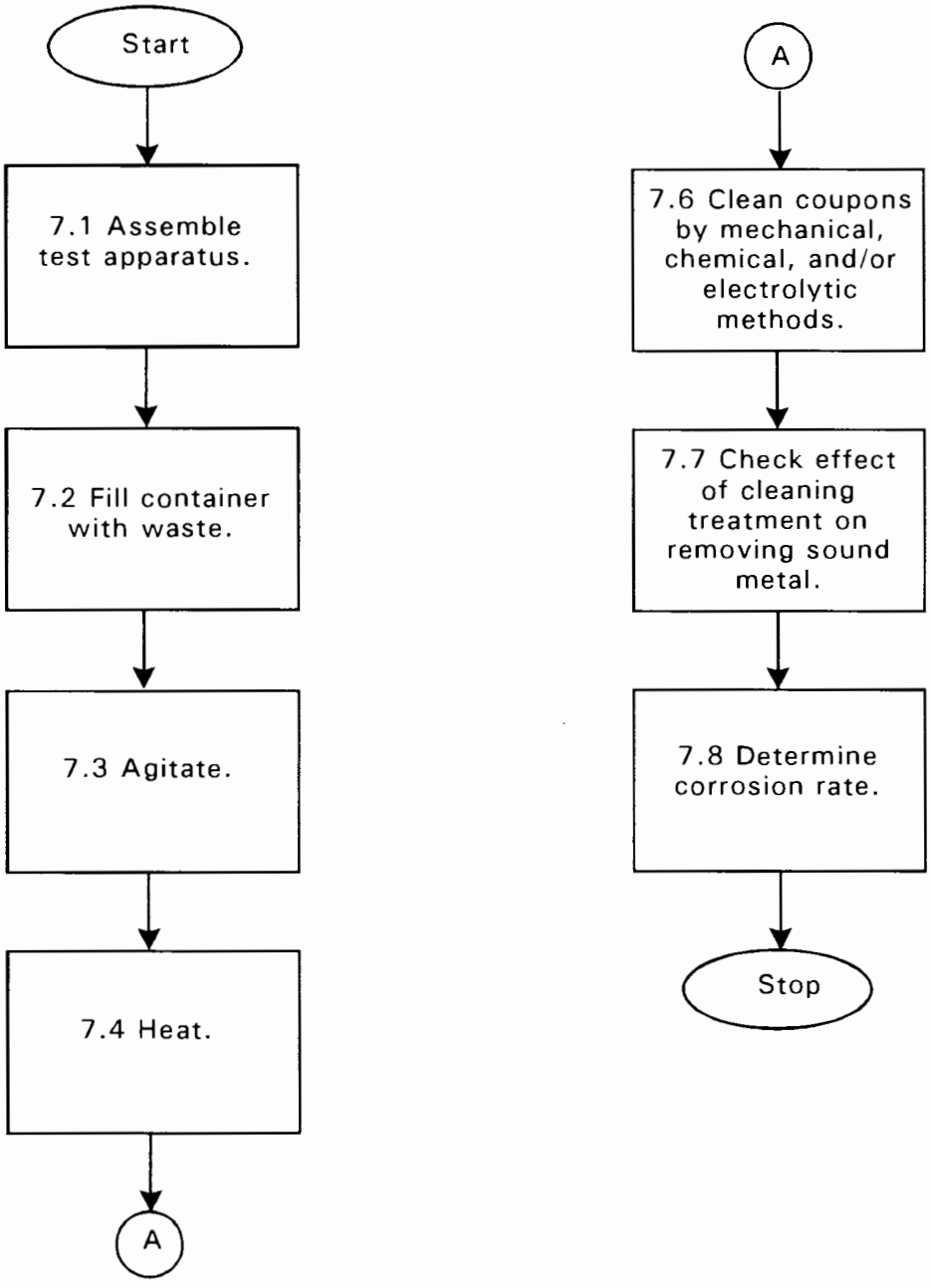
8.2 Duplicate samples should be analyzed on a routine basis.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. National Association of Corrosion Engineers, "Laboratory Corrosion Testing of Metals for the Process Industries," NACE Standard TM-01-69 (1972 Revision), NACE, 3400 West Loop South, Houston, TX 77027.


Start
7.1 Assemble test apparatus.
7.2 Fill container with waste.
7.3 Agitate.
7.4 Heat.
A
A
7.6 Clean coupons by mechanical, chemical, and/or electrolytic methods.
7.7 Check effect of cleaning treatment on removing sound metal.
7.8 Determine corrosion rate.
Stop

METHOD 1120

DERMAL CORROSION

1.0 SCOPE AND APPLICATION

1.1 The dermal corrosion assay system is an *in vitro* test method which determines the corrosive potential of a substance toward human skin. The method is simple, rapid, accurate, and may be applied to both solids, liquids and emulsions. The liquids may be aqueous or non-aqueous. Solids can be water-soluble or non-soluble. The samples may be pure chemicals, dilutions, formulations, or waste. No prior treatment of the sample is required. This method may be used to meet certain regulatory applications, e.g., DOT corrosivity measurement for Packing Groups, but is not required for determining if a waste passes or fails the characteristic of corrosivity per the RCRA definition.

1.2 This method is applicable to a limited number of materials, specifically: Acids, inorganic and organic; acid derivatives (anhydride, halo acids, salts, etc.), inorganic and organic; acyl halides; alkylamines and polyalkylamines; bases, inorganic and organic; chlorosilanes; and metal halides and oxyhalides.

2.0 SUMMARY OF METHOD

2.1 The assay system is an *in vitro* test method which is composed of two components, a synthetic macromolecular biobarrier and a Chemical Detection System (CDS). Test samples are applied on top of the macromolecular biobarrier. Corrosive samples are able to disrupt the macromolecular structure of the biobarrier. A color change in the CDS, located beneath the biobarrier, is detected visually and indicates that the test sample has altered the biobarrier sufficiently to allow its passage through the full thickness of the biobarrier. The time it takes a sample to disrupt the biobarrier is inversely proportional to the degree of corrosivity of the sample - the longer it takes to observe a color change, the less corrosive the substance is. Noncorrosive samples do not disrupt the biobarrier, or disrupt the biobarrier after a predetermined time period (see Section 2.4).

Corrosive samples may be placed into three different classes of corrosivity, established by the time required for the sample to break through the biobarrier. These classes are called Packing Groups by the U.S. Department of Transportation (DOT). Packing Groups are assigned according to the degree of danger presented by the corrosive material; Packing Group I indicates great danger; Packing Group II, medium danger; Packing Group III, minor danger. For consistency, these same definitions are used for this test method and are referred to as Group I, Group II, and Group III.

2.2 Prior to performing the assay, samples are pre-qualified to establish their compatibility with the assay system. The sample is placed in a small amount of CDS fluid. If any detectable change occurs in the CDS, the sample is qualified and can be analyzed by the test. If a sample is non-qualified, it is incompatible with the CDS and must be tested by another method.

2.3 Test samples are classified into categories by the screening test which is supplied with the assay kit. The category that a sample is assigned to will determine how the Groups will be assigned. Test samples are classified by pH changes produced in two well-defined buffers - one designed to buffer acids and another that buffers bases. These buffers are supplied as part of the screening test. Four different categories are defined as follows:

2.3.1 Category A_1 substances produce a large change in pH when they are added to the acid buffer. This change in pH is indicated by a strong color change of the acid buffer solution.

2.3.2 Category B_1 substances produce a large change in pH when they are added to the base buffer. This change in pH is indicated by a strong color change of the base buffer solution.

2.3.3 Category A_2 substances produce little or no pH changes when added to the acid buffer, and therefore, little or no color change in the buffer solution is observed.

2.3.4 Category B_2 substances produce little or no pH changes when added to the base buffer, and therefore, little or no color change in the buffer solution is observed.

2.4 Groups are assigned in the assay system by taking into account the category that is assigned to a sample by the screening test, and the time it takes to detect a color change in the CDS in the assay. Category A_1 and B_1 samples are assigned to Group I if a color change is observed between zero and three minutes, to Group II if a color change is observed after three minutes and up to one hour, and to Group III if a color change is observed after one hour and up to four hours. If no color change occurs in four hours, the chemical is classified as Noncorrosive.

Category A_2 and B_2 samples are assigned to Group I if a color change is observed between zero and three minutes, to Group II if a color change is observed after three minutes and up to 30 minutes, and to Group III if a color change is observed after 30 minutes and up to 60 minutes. If no color change occurs in 60 minutes, the chemical is classified as Noncorrosive.

3.0 INTERFERENCES

3.1 The test is not subject to interference from color, turbidity, colloidal matter or high salinity.

3.2 The Pre-qualification Test, the Screening Test and the Assay must be performed at room temperature. The samples must also be at room temperature (17- 25°C).

4.0 APPARATUS AND MATERIALS

4.1 Corrositex Assay Kit (InVitro International, 16632 Millikan Avenue, Irvine, CA 92714). The following three items are supplied in the Corrositex Assay Kit:

4.1.1 Four racks holding seven vials with black caps.

4.1.2 One tray of 24 membrane discs.

4.1.3 Four data sheets (color charts).

4.2 Combination hot plate/stir plate or equivalent - able to heat to 75°C. Stirring speed should be adjustable.

4.3 Digital thermometer - able to read to 75°C.

4.4 Timers (6) - able to measure hours, minutes and seconds.

4.5 Repeat pipettor - this pipet is different than the pipet specified in Section 4.12. Delivers 200 µL repeatedly, without refilling between individual deliveries.

4.6 2.5 mL combitip for repeat pipettor.

4.7 Lab Industries or equivalent sample pipettor - a positive displacement pipettor useful when pipetting viscous samples.

4.8 Pipet tips for Lab Industries, or equivalent, pipettor.

4.9 Test tubes

4.10 Balance - capable of weighing 100 mg accurately.

4.11 Spatula - capable of transferring 0.1 - 0.5 g.

4.12 Pipets - microliter, with disposable tips. Should be able to measure 100 µL accurately.

4.13 Tweezers.

4.14 Permanent marker pens.

4.15 Plastic wrap.

5.0 REAGENTS

5.1 All reagents listed below are provided in the Corrositex Assay Kit except for the positive and negative controls mentioned in Section 5.7. The Corrositex Assay Kit is available from InVitro International, 16632 Millikan Avenue, Irvine, CA 92714.

5.2 Chemical Detection System (CDS).

5.3 Screening test buffer solutions.

5.4 Confirmation Test Solution.

5.5 One gram of the biobarrier matrix and a microstir bar.

5.6 10 mL of biobarrier diluent.

5.7 Positive and negative controls, if desired, for GLP purposes.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Appropriate precautions should be taken for handling potentially corrosive substances such as wearing gloves and having proper eye protection.

6.2 Samples should be analyzed as soon as possible after collection.

7.0 PROCEDURE

7.1 Follow the established laboratory procedures for working with hazardous test samples. Wear lab coat, gloves and safety glasses when working with any potentially corrosive material.

7.2 Pre-Qualification Test

7.2.1 Add 100 mg or 150 µL of sample to 1.0 mL of CDS in duplicate test tubes.

7.2.1.1 Sample qualifies if there is a color reaction within 5 minutes: proceed with assay.

7.2.1.2 If no reaction is observed, the sample is non-qualified. Seek other methods to determine corrosivity.

7.3 Screening Test

7.3.1 Liquid samples

7.3.1.1 Add 150 µL of sample to Test Tubes A and B. Cap the test tubes and shake vigorously for 10 seconds. Read the color change of the mixture within one minute. If the sample is immiscible in the solution, wait one minute and then read the color change at the interface.

7.3.1.2 Assign the category. If an intense color change (similar to the Category 1 color chart) is observed in Tube A or Tube B, assign the sample to Category 1. If a less intense color change (similar to the Category 2 color chart) is observed in either Tube A or Tube B, assign the sample to Category 2 . If no color change is observed in either Tube A or Tube B, proceed to the next step.

7.3.1.3 Confirm test. Add two drops of the Confirm reagent to Tube B. Cap the test tube and shake vigorously for 5 seconds. The color of the solution will match one of the colors shown in the accompanying color chart, confirming that the sample is Category 2 material.

7.3.2 Solid samples

7.3.2.1 Add 100 mg of sample to Test Tubes A and B. Cap the test tubes and shake vigorously for one minute. Wait another minute and read the color change of the mixture. If the sample is insoluble in the solution, allow the mixture to settle and read the color change at the interface of the solution and the solid.

7.3.2.2 Assign the category. If an intense color change (similar to the Category 1 color chart) is observed in either Tube A or Tube B, assign the sample to Category 1. If a less intense color change (similar to the Category 2 color chart) is observed in either Tube A or Tube B, assign the sample to Category 2. If no color change is observed in either Tube A or Tube B, proceed to the next step.

7.3.2.3 Confirm test. Add two drops of the Confirm reagent to Tube B. Cap the test tube and shake vigorously for 5 seconds. The color of the solution will match one of the colors shown in the accompanying color chart, confirming that the sample is Category 2 material.

7.4 Assay

7.4.1 Biobarrier preparation

7.4.1.1 Biobarrier matrix preparation - must be completed at least two hours prior to running assay.

7.4.1.2 Place scintillation vial containing biobarrier matrix powder on the hot plate pad. Begin spinning the stir bar before adding the diluent.

7.4.1.3 Add the entire contents of the biobarrier diluent vial slowly and constantly to the vial of biobarrier matrix powder. Make sure that the stir bar is turning while adding the diluent. The stir bar should be turning rapidly, but not so fast that the solution foams.

7.4.1.4 Turn the heat on low; monitor the temperature of the solution as it is warming. Gradually increase the heat as necessary to warm the solution to 68°C (±1°C) to solubilize the matrix. This may take approximately 20 minutes. **DO NOT** allow the temperature to exceed 70°C.

7.4.1.5 While the solution is warming, remove the tray of 24 membrane discs from the refrigerator. Remove the tray lid.

7.4.1.6 After the biobarrier matrix solution reaches 68°C and has been completely solubilized, turn off the heat and move the vial toward the edge of the heat pad to keep it warm while aliquotting into the membrane discs.

7.4.1.7 Dispense solubilized solution into membrane discs. Using the repeat pipettor, set to dispense 200 µL. Slowly fill the pipette tip with biobarrier solution, avoiding air bubbles. Dispense one aliquot back into the biobarrier vial to ensure proper subsequent volume delivery. Wipe the tip before dispensing each aliquot. Dispense 200 µL into each disc, ensuring that the entire membrane is covered and no air bubbles have formed. Any air bubbles in the gel will alter the results of the test, therefore the disc cannot be used.

7.4.1.8 Label the lid with the date, time, lot number, and initials of the technician preparing the biobarrier. Wrap the filled tray evenly with plastic wrap; do not bunch up the plastic wrap underneath the plate.

7.4.1.9 Store the tray at 2 - 8°C for at least two hours before beginning any testing. The biobarrier is stable for seven days if wrapped and stored at 2 - 8°C.

7.4.2 Running the assay.

7.4.2.1 On the data sheet, complete the lot number, date, time, name of technician, name of chemical, whether it is solid or liquid, and pH of a 10% solution diluted in water or appropriate solvent.

7.4.2.2 When ready to test, remove one tray of seven pre-filled black-capped scintillation vials from the kit box.

7.4.2.3 Remove the tray of 24 membrane discs from the refrigerator. Place on a tray of ice.

7.4.2.4 Place disc into first scintillation vial. Do not allow the discs to be in contact with the CDS for longer than two minutes before applying the test sample. Within two minutes, add 500 µL (using the Lab Industries pipettor, or equivalent) or 500 mg (using spatula or tweezers) of test sample to disc. Start timer the instant the sample is added.

Note: Do not cap the vials while test is in progress due to potential pressure build-up.

7.4.2.5 Watch the vial for three minutes, ensuring that the color reaction is not missed if it is a Group I sample. Changes in the CDS may include various color changes, flaking or precipitation.

7.4.2.6 Add three more discs and samples to vials, staggering each start time so that the most accurate reaction times are recorded.

7.4.2.7 Allow assay to run until color or physical reaction occurs. Category 1 samples should be checked for reactions at 3 minutes, 1 hour and 4 hours. Category 2 samples should be checked for reactions at 3, 30 and 60 minutes.

7.4.2.8 At the first indication of the presence of a chemical reaction in the CDS, there will be a color change produced beneath the bottom-center of each biobarrier disc. As soon as a reaction is observed, immediately record net time of each vial on the data sheet.

7.4.2.9 Run positive and negative controls in the other two vials, if desired, for GLP purposes.

7.4.3 Assignment of Groups.

7.4.3.1 Category 1 samples are assigned to Group I if a color change is observed between zero and three minutes, to Group II if a color change is observed after three minutes and up to one hour, and to Group III if a color change is observed after one hour and up to four hours. If no color change occurs in four hours, the chemical is classified as Noncorrosive.

7.4.3.2 Category 2 samples are assigned to Group I if a color change is observed between zero and three minutes, to Group II if a color change is observed after three minutes and up to 30 minutes, and to Group III if a color change is observed after 30 minutes and up to 60 minutes. If no color change occurs in 60 minutes, the chemical is classified as Noncorrosive.

8.0 QUALITY CONTROL

8.1 Samples should be analyzed in quadruplicate. The test may be analyzed in duplicate if a simple screening of corrosives and noncorrosives is all that is required. However, it is recommended that for greater accuracy, samples be analyzed in quadruplicate. It is suggested that positive and negative controls be analyzed to conform with GLP.

9.0 METHOD PERFORMANCE

9.1 Interlaboratory and intralaboratory studies were conducted with five different laboratories. Ten different chemicals were tested with six replicates. The data are presented in Table 1.

9.2 More than 200 data points have been collected at InVitro International for six reference samples. Statistical analysis of this data shows the standard deviation for ethylenediamine and ferric chloride is about 5% of their respective assay times, and about 10% for maleic anhydride, sodium hydroxide, and dicyclohexylamine. The standard deviation for sulfuric acid approaches 18% of its assay time, but when taken into account that the mean assay time is less than 1 minute, a standard deviation of 0.13 minutes is actually a reflection of the difficulty of measuring such brief time periods.

9.3 The Corrositex assay has been used by more than 300 laboratories to test approximately 4,000 test materials in its first phase of utilization in industry. Diverse chemicals and formulations which include liquids, solids, insolubles and immiscibles have been studied from many major industries including petrochemical, agrochemical, surfactant, textile, paper and pulp, electroplating and water treatment. Examples of dermal corrosion values compared to pH for selected compounds are shown in Table 2.

9.4 Data results from 1,050 samples that have been tested using the assay system were complied and compared with *in vivo* data. Ninety-two percent of the samples (965 samples) passed the Pre-qualification Test and were then analyzed in the screening test and the assay. Assay was found to be highly concordant with corrosive/noncorrosive *in vivo* results. Of 406 corrosive samples with *in vivo* data, 377 (93%) were correctly identified as corrosive by assay. Of 296 noncorrosive samples with *in vivo* data, 83% were identified as noncorrosives, demonstrating the ability of this *in vitro* method to correctly identify corrosives and noncorrosives. Assay was also shown to accurately predict Packing Groups. Six hundred out of 702 samples (85.5%) were placed in the same Packing Group as that indicated by *in vivo* testing. Only 38 test samples out of 702 samples that had *in vivo* data were found to underestimate (5.4%). Of these 38 samples, 28 were distinct samples and the remainder were samples that had been tested in more than one laboratory. When taking this information into account, the percent of underestimation decreased to about 4%.

10.0 REFERENCES

1. Code of Federal Regulations, Transportation Title 49, Hazardous Materials Table, Section 172.101 (1991).

2. Code of Federal Regulations, Transportation Title 49, Method of Testing Corrosion to the Skin, Part 173, Appendix A (1991).

3. Schlesselman, J.J. (1973) Planning a Longitudinal Study: I. Sample Size Determination. J. Chron. Dis. **26**, 553-560.

4. ASTM Standards on Precision and Bias for Various Applications, “Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method”; ASTM: Philadelphia, PA, 1992; E 691-92.

5. Gordon, V.C., Harvell, J., and Maibach, H. (1994). Dermal Corrosion, The Corrositex System, A DOT Accepted Method to Predict Corrosivity of Test Materials. *In Vitro* Toxicology. Ed. Mary Ann Liebert, 1994.

TABLE 1
LABORATORY DATA

Dichloroacetyl chloride

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	3.30	0.59	17.88%
2	2.99	0.30	10.03%
3	3.88	0.47	12.11%
4	2.50	0.26	10.40%
5	3.30	0.28	8.48%

Formic acid

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	6.32	0.51	8.07%
2	5.08	0.46	9.06%
3	5.18	0.77	14.86%
4	4.82	0.29	6.02%
5	4.02	0.29	7.21%

Dichloroacetic acid

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	6.92	0.32	4.62%
2	5.21	0.25	4.80%
3	6.32	0.98	15.51%
4	5.78	0.26	4.50%
5	5.65	0.46	8.14%

Chloroacetic acid

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	5.46	0.36	6.59%
2	7.83	0.00	0.00%
3	4.95	0.35	7.07%
4	6.91	0.94	13.60%
5	4.95	0.34	6.87%

TABLE 1 (continued)

Dodecyltrichlorosilane

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	10.78	0.05	0.46%
2	11.59	0.36	3.11%
3	11.22	0.82	7.31%
4	11.96	0.56	4.68%
5	10.98	0.29	2.64%

Ammonium hydrogen sulfate

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	10.47	0.56	5.35%
2	9.02	0.33	3.66%
3	13.82	1.0	7.24%
4	11.17	0.93	8.33%
5	7.88	0.26	3.30%

Ethylenediamine

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	17.24	0.38	2.20%
2	21.33	0.53	2.48%
3	26.12	1.30	4.98%
4	20.76	0.19	0.92%
5	22.48	1.40	6.23%

Aluminum chloride

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	11.91	0.41	3.44%
2	21.33	0.53	2.48%
3	26.12	1.30	4.98%
4	20.76	0.19	0.92%
5	22.48	1.40	6.23%

TABLE 1 (continued)

Acetic acid

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	28.52	0.87	3.05%
2	27.00	0.00	0.00%
3	34.98	0.22	0.63%
4	36.30	0.41	1.13%
5	29.67	0.62	2.09%

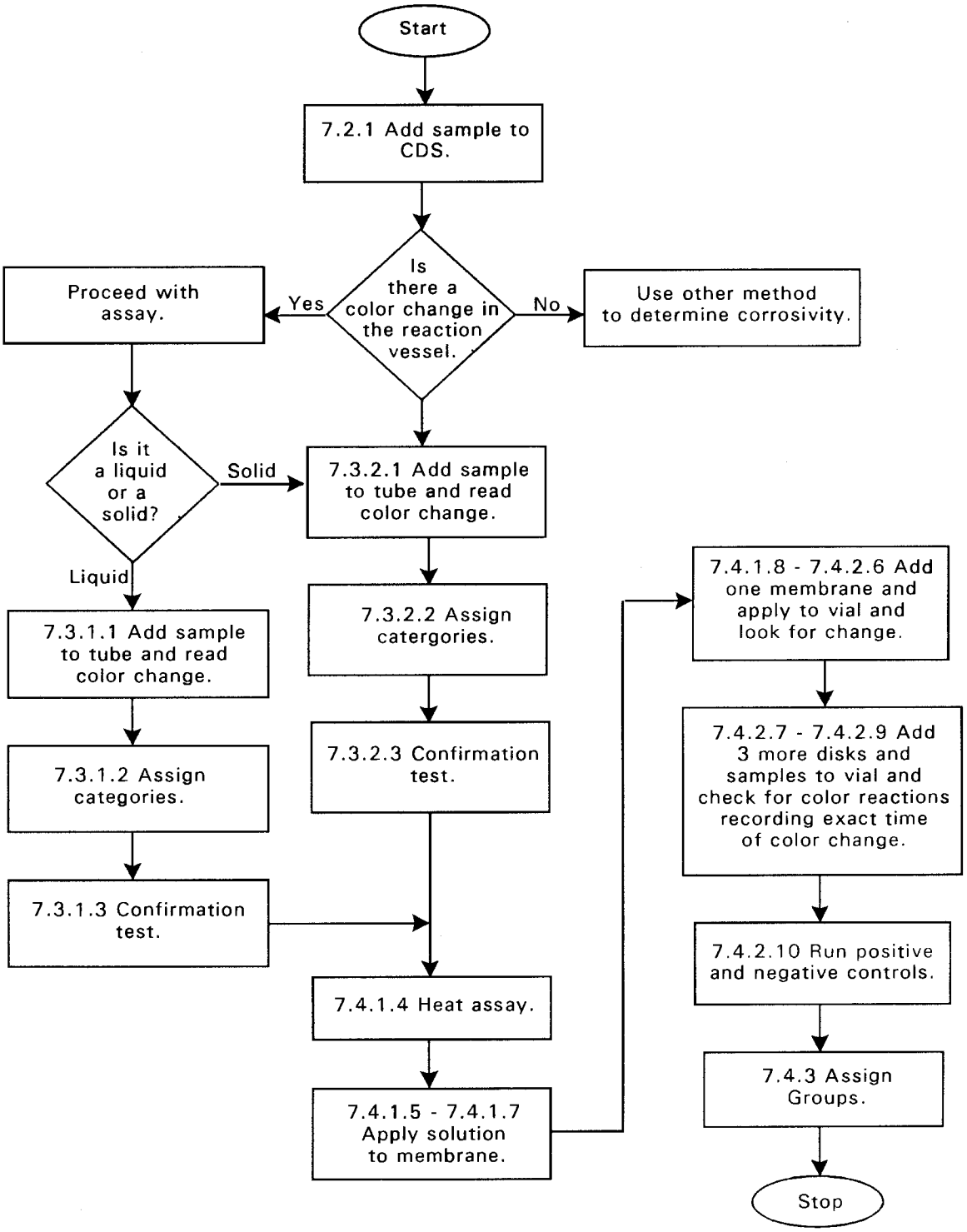
Dicyclohexylamine

Laboratory	Mean of 6 Test Results (minutes)	Standard Deviation	Relative Standard Deviation
1	181.73	0.47	0.26%
2	168.83	9.11	5.40%
3	210.70	7.68	3.64%
4	159.04	7.58	4.77%
5	126.75	0.62	0.49%

TABLE 2. EXAMPLES OF DERMAL CORROSION VALUES FOR SELECTED COMPOUNDS

Compound Name	Concentration (weight %)	pH[1]	Time (minutes)
Acetic acid	99+	0.00	29.31
Aluminum chloride	pure	2.92	16.50
Ammonium hydroxide	10.00	12.37	5.41
Bromoacetic acid	55.60	0.93	9.17
Butylamine	40.00	12.96	>240
Citric acid	20.00	1.28	47.65
1,2-Diaminopropane	99+	12.06	21.67
Dichloroacetic acid	3.10	0.98	37.63
Dicyclohexylamine	99.00	9.57	210.00
Diethylamine	98.00	13.86	5.89
Diethylene triamine	99.00	12.01	34.00
Ethanolamine	99+	11.82	21.68
Ferric chloride	98.00	3.00	21.30
Formic acid	33.90	0.62	>240
Hydrochloric acid	35.00	0.00	5.80
Hexanoic acid	99.00	3.00	149.00
Maleic acid	99.00	1.30	15.55
Mercaptoacetic acid	15.10	1.60	42.09
Nitric acid	90.00	0.00	0.57
Phosphoric acid	85.00	0.00	15.00
Potassium hydroxide	pellets	14.00	6.82
Propionic acid	99+	0.35	34.59
Sodium hydroxide	pellets	13.81	14.67
Sodium metasilicate	20.00	13.28	17.17
Sulfuric acid	15.00	0.00	11.48
Thiophosphoryl chloride	98.00	5.81	10.13
Tributylamine	99+	10.70	>240
Trichlorotoluene	99.00	3.32	>240
Triethanolamine	60.00	11.02	41.03
Triphosphoryl chloride	98.00	5.80	10.25

[1] pH of a 10% solution of the compound in water.


Start
7.2.1 Add sample to CDS.
Is there a color change in the reaction vessel.
Yes
No
Use other method to determine corrosivity.
Proceed with assay.
Is it a liquid or a solid?
Solid
Liquid
7.3.2.1 Add sample to tube and read color change.
7.3.2.2 Assign catergories.
7.3.2.3 Confirmation test.
7.3.1.1 Add sample to tube and read color change.
7.3.1.2 Assign categories.
7.3.1.3 Confirmation test.
7.4.1.4 Heat assay.
7.4.1.5 - 7.4.1.7 Apply solution to membrane.
7.4.1.8 - 7.4.2.6 Add one membrane and apply to vial and look for change.
7.4.2.7 - 7.4.2.9 Add 3 more disks and samples to vial and check for color reactions recording exact time of color change.
7.4.2.10 Run positive and negative controls.
7.4.3 Assign Groups.
Stop

METHOD 1310A

EXTRACTION PROCEDURE (EP) TOXICITY TEST METHOD AND STRUCTURAL INTEGRITY TEST

1.0 SCOPE AND APPLICATION

1.1 This method is an interim method to determine whether a waste exhibits the characteristic of Extraction Procedure Toxicity.

1.2 The procedure may also be used to simulate the leaching which a waste may undergo if disposed of in a sanitary landfill. Method 1310 is applicable to liquid, solid, and multiphase samples.

2.0 SUMMARY OF METHOD

2.1 If a representative sample of the waste contains > 0.5% solids, the solid phase of the sample is ground to pass a 9.5 mm sieve and extracted with deionized water which is maintained at a pH of 5 $\pm$ 0.2, with acetic acid. Wastes that contain < 0.5% filterable solids are, after filtering, considered to be the EP extract for this method. Monolithic wastes which can be formed into a cylinder 3.3 cm (dia) x 7.1 cm, or from which such a cylinder can be formed which is representative of the waste, may be evaluated using the Structural Integrity Procedure instead of being ground to pass a 9.5-mm sieve.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - For purposes of this test, an acceptable extractor is one that will impart sufficient agitation to the mixture to (1) prevent stratification of the sample and extraction fluid and (2) ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. Examples of suitable extractors are shown in Figures 1-3 of this method and are available from: Associated Designs & Manufacturing Co., Alexandria, Virginia; Glas-Col Apparatus Co., Terre Haute, Indiana; Millipore, Bedford, Massachusetts; and Rexnard, Milwaukee, Wisconsin.

4.2 pH meter or pH controller - Accurate to 0.05 pH units with temperature compensation.

4.3 Filter holder - Capable of supporting a 0.45-µm filter membrane and of withstanding the pressure needed to accomplish separation. Suitable filter holders range from simple vacuum units to relatively complex systems that can exert up to 5.3 kg/cm^3 (75 psi) of pressure. The type of filter holder used depends upon the properties of the mixture to be filtered. Filter holders known to EPA and deemed suitable for use are listed in Table 1.

4.4 Filter membrane - Filter membrane suitable for conducting the required filtration shall be fabricated from a material that (1) is not physically changed by the waste material to be filtered and (2) does not absorb or leach the chemical species for which a waste's EP extract will be analyzed. Table 2 lists filter media known to the agency to be suitable for solid waste testing.

4.4.1 In cases of doubt about physical effects on the filter, contact the filter manufacturer to determine if the membrane or the prefilter is adversely affected by the particular waste. If no information is available, submerge the filter in the waste's liquid phase. A filter that undergoes visible physical change after 48 hours (i.e., curls, dissolves, shrinks, or swells) is unsuitable for use.

4.4.2 To test for absorption or leaching by the filter:

4.4.2.1 Prepare a standard solution of the chemical species of interest.

4.4.2.2 Analyze the standard for its concentration of the chemical species.

4.4.2.3 Filter the standard and reanalyze. If the concentration of the filtrate differs from that of the original standard, then the filter membrane leaches or absorbs one or more of the chemical species and is not usable in this test method.

4.5 Structural integrity tester - A device meeting the specifications shown in Figure 4 and having a 3.18-cm (1.25-in) diameter hammer weighing 0.33 kg (0.73 lb) with a free fall of 15.24 cm (6 in) shall be used. This device is available from Associated Design and Manufacturing Company, Alexandria, VA 22314, as Part No. 125, or it may be fabricated to meet these specifications.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Acetic acid (0.5N), CH_3COOH. This can be made by diluting concentrated glacial acetic acid (17.5N) by adding 57 mL glacial acetic acid to 1,000 mL of water and diluting to 2 liters. The glacial acetic acid must be of high purity and monitored for impurities.

5.4 Analytical standards should be prepared according to the applicable analytical methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Preservatives must not be added to samples.

6.3 Samples can be refrigerated if it is determined that refrigeration will not affect the integrity of the sample.

7.0 PROCEDURE

7.1 If the waste does not contain any free liquid, go to Step 7.9. If the sample is liquid or multiphase, continue as follows. Weigh filter membrane and prefilter to $\pm$ 0.01 g. Handle membrane and prefilters with blunt curved-tip forceps or vacuum tweezers, or by applying suction with a pipet.

7.2 Assemble filter holder, membranes, and prefilters following the manufacturer's instructions. Place the 0.45-µm membrane on the support screen and add prefilters in ascending order of pore size. Do not prewet filter membrane.

7.3 Weigh out a representative subsample of the waste (100 g minimum).

7.4 Allow slurries to stand, to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.

7.5 Wet the filter with a small portion of the liquid phase from the waste or from the extraction mixture. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops. This liquid will constitute part or all of the extract (refer to Step 7.16). The liquid should be refrigerated until time of analysis.

NOTE: Oil samples or samples containing oil are treated in exactly the same way as any other sample. The liquid portion of the sample is filtered and treated as part of the EP extract. If the liquid portion of the sample will not pass through the filter (usually the case with heavy oils or greases), it should be carried through the EP extraction as a solid.

7.6 Remove the solid phase and filter media and, while not allowing them to dry, weigh to $\pm$ 0.01 g. The wet weight of the residue is determined by calculating the weight difference between the weight of the filters (Step 7.1) and the weight of the solid phase and the filter media.

7.7 The waste will be handled differently from this point on, depending on whether it contains more or less than 0.5% solids. If the sample appears to have < 0.5% solids, determine the percent solids exactly (see Note below) by the following procedure:

7.7.1 Dry the filter and residue at 80°C until two successive weighings yield the same value.

7.7.2 Calculate the percent solids, using the following equation:

$$\frac{\text{weight of filtered solid and filters} - \text{tared weight of filters}}{\text{initial weight of waste material}} \times 100 = \% \text{ solids}$$

NOTE: This procedure is used only to determine whether the solid must be extracted or whether it can be discarded unextracted. It is not used in calculating the amount of water or acid to use in the extraction step. Do not extract solid material that has been dried at 80°C. A new sample will have to be used for extraction if a percent solids determination is performed.

7.8 If the solid constitutes < 0.5% of the waste, discard the solid and proceed immediately to Step 7.17, treating the liquid phase as the extract.

7.9 The solid material obtained from Step 7.5 and all materials that do not contain free liquids shall be evaluated for particle size. If the solid material has a surface area per g of material $\geq$ 3.1 cm^2 or passes through a 9.5-mm (0.375-in.) standard sieve, the operator shall proceed to Step 7.11. If the surface area is smaller or the particle size larger than specified above, the solid material shall be prepared for extraction by crushing, cutting, or grinding the material so that it passes through a 9.5-mm (0.375-in.) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described in Step 7.10.

7.10 Structural Integrity Procedure (SIP)

7.10.1 Cut a 3.3-cm diameter by 7.1-cm long cylinder from the waste material. If the waste has been treated using a fixation process, the waste may be cast in the form of a cylinder and allowed to cure for 30 days prior to testing.

7.10.2 Place waste into sample holder and assemble the tester. Raise the hammer to its maximum height and drop. Repeat 14 additional times.

7.10.3 Remove solid material from tester and scrape off any particles adhering to sample holder. Weigh the waste to the nearest 0.01 g and transfer it to the extractor.

7.11 If the sample contains > 0.5% solids, use the wet weight of the solid phase (obtained in Step 7.6) to calculate the amount of liquid and acid to employ for extraction by using the following equation:

$$W = W_f - W_t$$

where :

W = Wet weight in g of solid to be charged to extractor.

W_f = Wet weight in g of filtered solids and filter media.

W_t = Weight in g of tared filters.

If the waste does not contain any free liquids, 100 g of the material will be subjected to the extraction procedure.

7.12 Place the appropriate amount of material (refer to Step 7.11) into the extractor and add 16 times its weight with water.

7.13 After the solid material and water are placed in the extractor, the operator shall begin agitation and measure the pH of the solution in the extractor. If the pH is > 5.0, the pH of the solution should be decreased to 5.0 $\pm$ 0.2 by slowly adding 0.5N acetic acid. If the pH is $\leq$ 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction, and, if the pH rises above 5.2, 0.5N acetic acid should be added to bring the pH down to 5.0 $\pm$ 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 mL of acid per g of solid. The mixture should be agitated for 24 hours and maintained at 20-40°C (68-104°F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller, manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123, or its equivalent, in conjunction with a metering pump and reservoir of 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed.

NOTE: Do not add acetic acid too quickly. Lowering the pH to below the target concentration of 5.0 could affect the metal concentrations in the leachate.

7.13.1 A pH meter should be calibrated in accordance with the manufacturer's specifications.

7.13.2 The pH of the solution should be checked, and, if necessary, 0.5 N acetic acid should be manually added to the extractor until the pH reaches 5.0 $\pm$ 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-minute intervals, moving to the next longer interval if the pH does not have to be adjusted > 0.5 pH units.

7.13.3 The adjustment procedure should be continued for at least 6 hours.

7.13.4 If, at the end of the 24-hour extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 mL per g of solids) has not been added, the pH should be adjusted to 5.0 $\pm$ 0.2 and the extraction continued for an additional 4 hours, during which the pH should be adjusted at 1-hour intervals.

7.14 At the end of the extraction period, water should be added to the extractor in an amount determined by the following equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = mL water to be added.

W = Weight in g of solid charged to extractor.

A = mL of 0.5N acetic acid added during extraction.

7.15 The material in the extractor should be separated into its component liquid and solid phases in the following manner:

7.15.1 Allow slurries to stand to permit the solid phase to settle (wastes that are slow to settle may be centrifuged prior to filtration) and set up the filter apparatus (refer to Steps 4.3 and 4.4).

7.15.2 Wet the filter with a small portion of the liquid phase from the waste or from the extraction mixture. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops.

7.16 The liquids resulting from Steps 7.5 and 7.15 should be combined. This combined liquid (or waste itself, if it has < 0.5% solids, as noted in Step 7.8) is the extract.

7.17 The extract is then prepared and analyzed using the appropriate analytical methods described in Chapters Three and Four of this manual.

NOTE: If the EP extract includes two phases, concentration of contaminants is determined by using a simple weighted average. For example: An EP extract contains 50 mL of oil and 1,000 mL of an aqueous phase. Contaminant concentrations are determined for each phase. The final contamination concentration is taken to be:

$$\frac{\left(50 \times \text{contaminant conc. in oil}\right) + \left(1{,}000 \times \text{contaminant conc. of aqueous phase}\right)}{1050}$$

NOTE: In cases where a contaminant was not detected, use the MDL in the calculation. For example, if the MDL in the oily phase is 100 mg/L and 1 mg/L in the aqueous phase, the reporting limit would be 6 mg/L (rounded to the nearest mg). If the regulatory threshold is 5 mg/L, the waste may be EP toxic and results of the analysis are inconclusive.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 All quality control measures described in Chapter One and in the referenced analytical methods should be followed.

9.0 METHOD PERFORMANCE

9.1 The data tabulated in Table 3 were obtained from records of state and contractor laboratories and are intended to show the precision of the entire method (1310 plus analysis method).

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. EPA-APPROVED FILTER HOLDERS

Manufacturer	Size	Model No.	Comments
Vacuum Filters			
Gelman	47 mm	4011	
Nalgene	500 mL	44-0045	Disposable plastic unit, including prefilter, filter pads, and reservoir; can be used when solution is to be analyzed for inorganic constituents.
Nuclepore	47 mm	410400	
Millipore	47 mm	XX10 047 00	
Pressure Filters			
Nuclepore	142 mm	425900	
Micro Filtration Systems	142 mm	302300	
Millipore	142 mm	YT30 142 HW	

TABLE 2. EPA-APPROVED FILTRATION MEDIA

Supplier	Filter to be used for aqueous systems	Filter to be used for organic systems
Coarse prefilter		
Gelman	61631, 61635	61631, 61635
Nuclepore	210907, 211707	210907, 211707
Millipore	AP25 035 00, AP25 127 50	AP25 035 00, AP25 127 50
Medium prefilters		
Gelman	61654, 61655	
Nuclepore	210905, 211705	210905, 211705
Millipore	AP20 035 00, AP20 124 50	AP20 035 00, AP20 124 50
Fine prefilters		
Gelman	64798, 64803	64798, 64803
Nuclepore	210903, 211703	210903, 211703
Millipore	AP15 035 00, AP15 124 50	AP15 035 00, AP15 124 50
Fine filters (0.45 µm)		
Gelman	63069, 66536	60540 or 66149, 66151
Pall	NX04750, NX14225	
Nuclepore	142218	142218[a]
Millipore	HAWP 047 00, HAWP 142 50	FHUP 047 00, FHLP 142 50
Selas	83485-02, 83486-02	83485-02, 83486-02

[a]Susceptible to decomposition by certain polar organic solvents.

TABLE 3. PRECISIONS OF EXTRACTION-ANALYSIS PROCEDURES FOR SEVERAL ELEMENTS

Element	Sample Matrix	Analysis Method	Laboratory Replicates
Arsenic	1. Auto fluff	7060	1.8, 1.5 µg/L
	2. Barrel sludge	7060	0.9, 2.6 µg/L
	3. Lumber treatment company sediment	7060	28, 42 mg/L
Barium	1. Lead smelting emission control dust	6010	0.12, 0.12 mg/L
	2. Auto fluff	7081	791, 780 µg/L
	3. Barrel sludge	7081	422, 380 µg/L
Cadmium	1. Lead smelting emission control dust	3010/7130	120, 120 mg/L
	2. Wastewater treatment sludge from electroplating	3010/7130	360, 290 mg/L
	3. Auto fluff	7131	470, 610 µg/L
	4. Barrel sludge	7131	1100, 890 µg/L
	5. Oil refinery tertiary pond sludge	7131	3.2, 1.9 µg/L
Chromium	1. Wastewater treatment sludge from electroplating	3010/7190	1.1, 1.2 mg/L
	2. Paint primer	7191	61, 43 µg/L
	3. Paint primer filter	7191	--
	4. Lumber treatment company sediment	7191	0.81, 0.89 mg/L
	5. Oil refinery tertiary pond sludge	7191	--
Mercury	1. Barrel sludge	7470	0.15, 0.09 µg/L
	2. Wastewater treatment sludge from electroplating	7470	1.4, 0.4 µg/L
	3. Lead smelting emission control dust	7470	0.4, 0.4 µg/L

TABLE 3 (Continued)

Element	Sample Matrix	Analysis Method	Laboratory Replicates
Lead	1. Lead smelting emission control dust	3010/7420	940, 920 mg/L
	2. Auto fluff	7421	1540, 1490 µg/L
	3. Incinerator ash	7421	1000, 974 µg/L
	4. Barrel sludge	7421	2550, 2800 µg/L
	5. Oil refinery tertiary pond sludge	7421	31, 29 µg/L
Nickel	1. Sludge	7521	2260, 1720 µg/L
	2. Wastewater treatment sludge from electroplating	3010/7520	130, 140 mg/L
Chromium(VI)	1. Wastewater treatment sludge from electroplating	7196	18, 19 µg/L

FIGURE 1.
EXTRACTOR

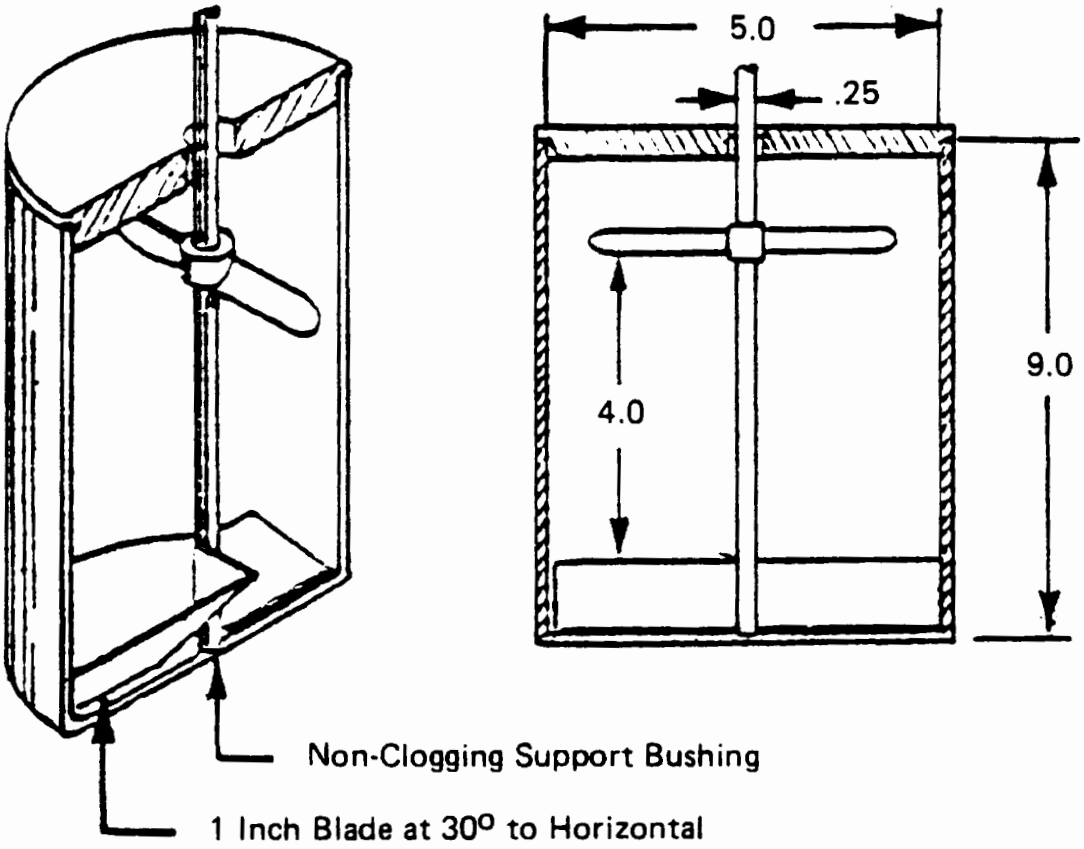


FIGURE 2.
ROTARY EXTRACTOR

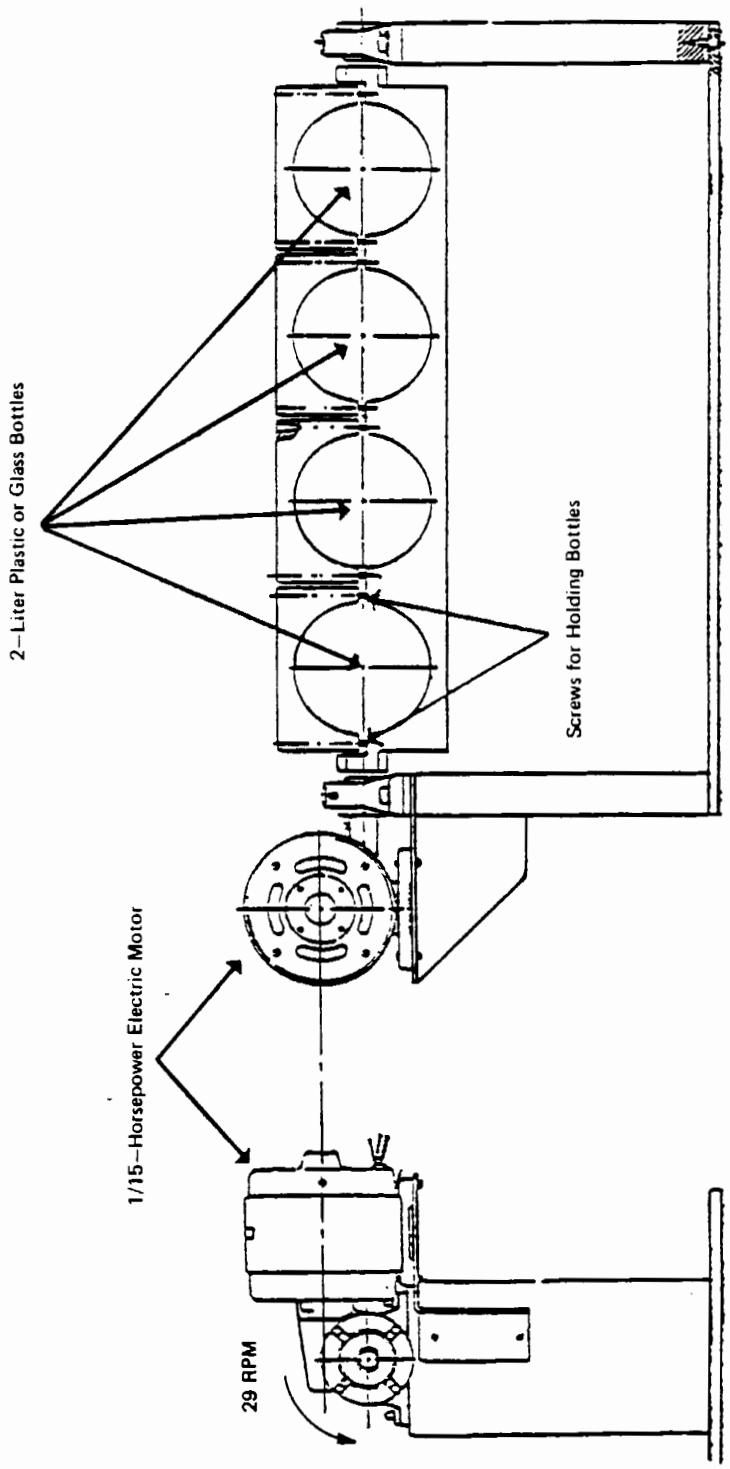


FIGURE 3.
EPRI EXTRACTOR

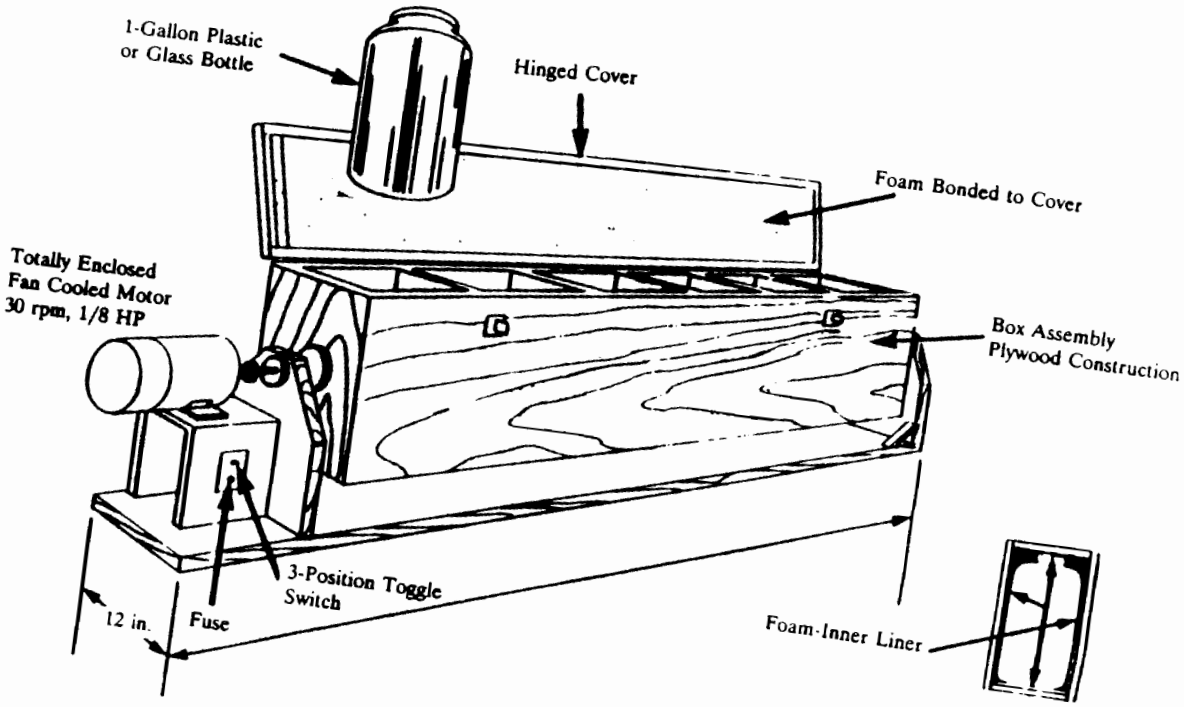
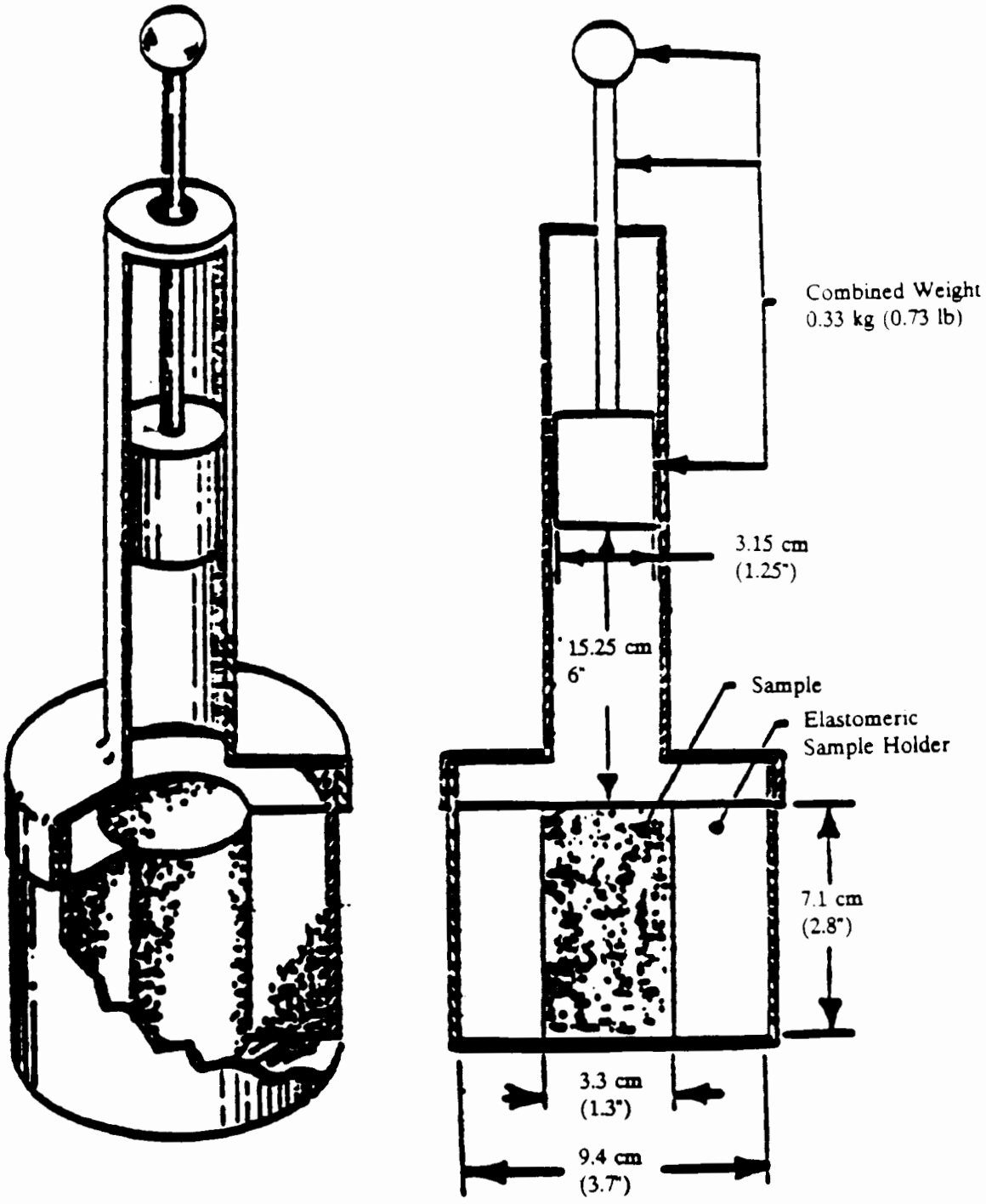
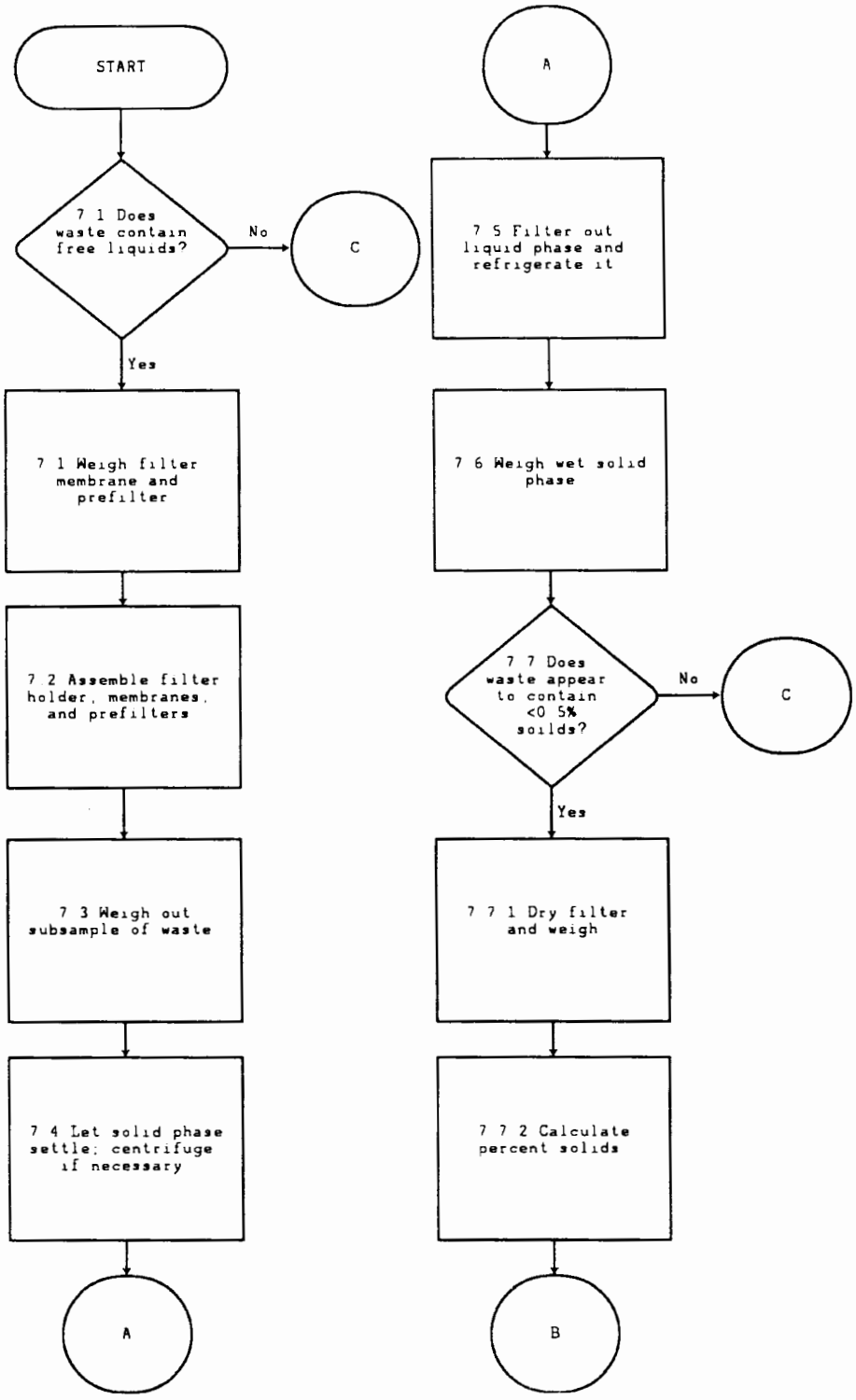
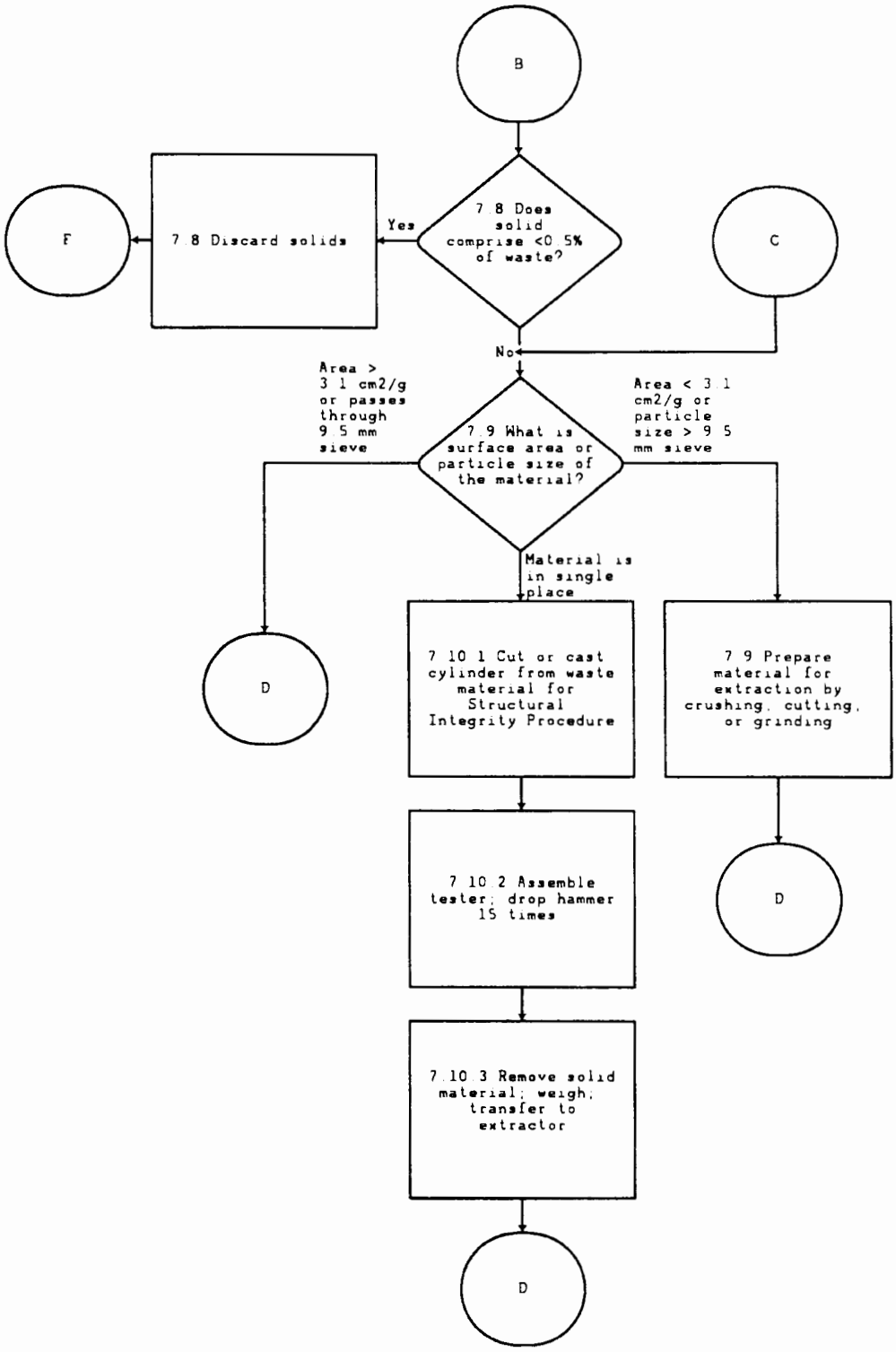
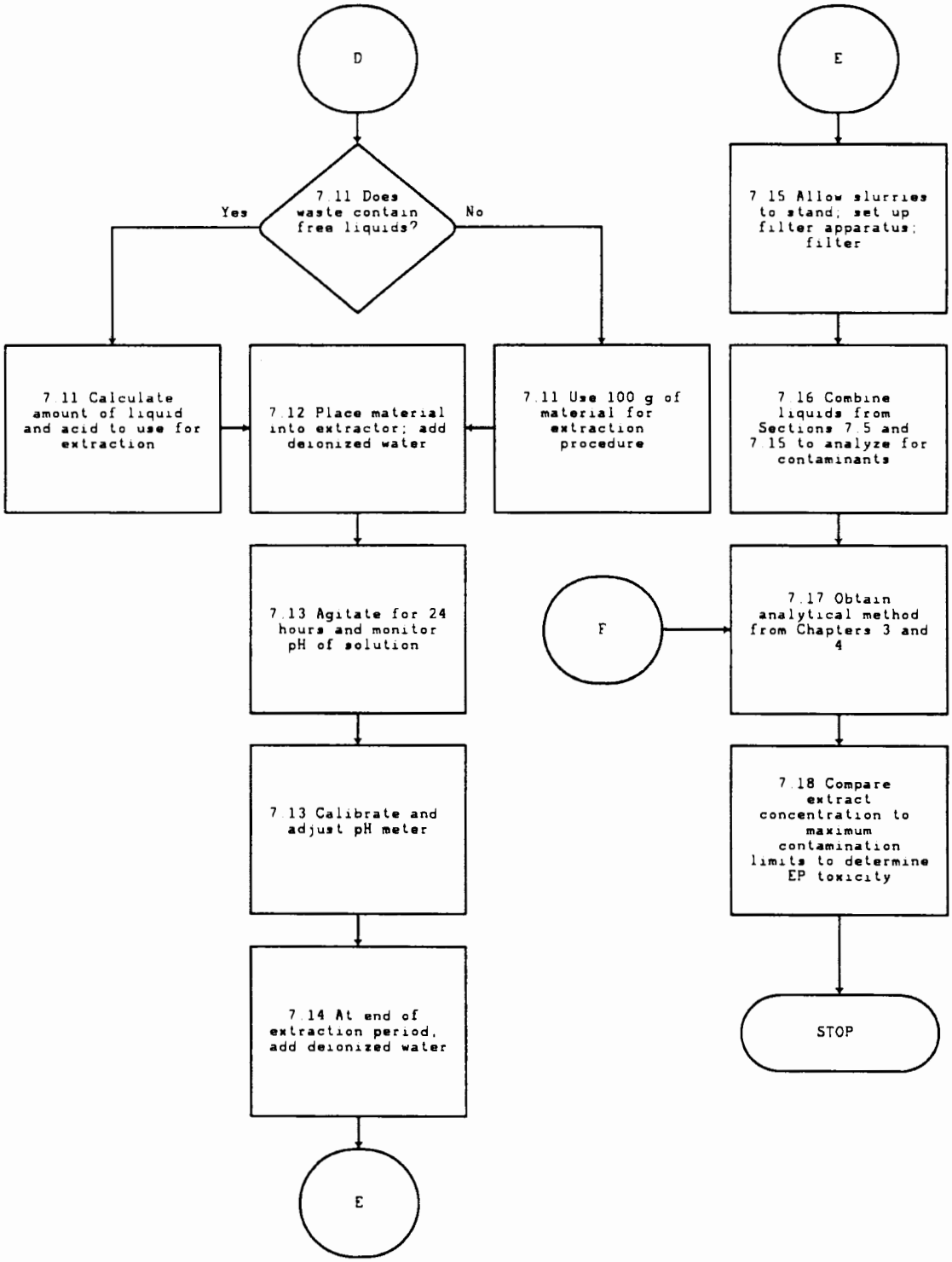


FIGURE 4.
COMPACTION TESTER




START
7 1 Does waste contain free liquids?
No
C
Yes
7 1 Weigh filter membrane and prefilter
7 2 Assemble filter holder, membranes, and prefilters
7 3 Weigh out subsample of waste
7 4 Let solid phase settle; centrifuge if necessary
A
A
7 5 Filter out liquid phase and refrigerate it
7 6 Weigh wet solid phase
7 7 Does waste appear to contain <0 5% solids?
No
C
Yes
7 7 1 Dry filter and weigh
7 7 2 Calculate percent solids
B


B
7.8 Does solid comprise <0.5% of waste?
Yes
7.8 Discard solids
F
C
No
7.9 What is surface area or particle size of the material?
Area > 3.1 cm2/g or passes through 9.5 mm sieve
Area < 3.1 cm2/g or particle size > 9.5 mm sieve
Material is in single place
D
7.10.1 Cut or cast cylinder from waste material for Structural Integrity Procedure
7.9 Prepare material for extraction by crushing, cutting, or grinding
7.10.2 Assemble tester; drop hammer 15 times
D
7.10.3 Remove solid material; weigh; transfer to extractor
D


D
7.11 Does waste contain free liquids?
Yes
No
7.11 Calculate amount of liquid and acid to use for extraction
7.12 Place material into extractor; add deionized water
7.11 Use 100 g of material for extraction procedure
7.13 Agitate for 24 hours and monitor pH of solution
7.13 Calibrate and adjust pH meter
7.14 At end of extraction period, add deionized water
E
E
7.15 Allow slurries to stand; set up filter apparatus; filter
7.16 Combine liquids from Sections 7.5 and 7.15 to analyze for contaminants
F
7.17 Obtain analytical method from Chapters 3 and 4
7.18 Compare extract concentration to maximum contamination limits to determine EP toxicity
STOP

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 SUMMARY OF METHOD

2.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

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[1] VITON® is a trademark of Du Pont.

4.2.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosili-

cate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 µm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25 °C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

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[2] TEDLAR® is a registered trademark of Du Pont.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 $\pm$ 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.4 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.5 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.6 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.7 Extraction fluid.

5.7.1 Extraction fluid # 1: Add 5.7 mL glacial CH_3CH_2OOH to 500 mL of reagent water (See Section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 $\pm$ 0.05.

5.7.2 Extraction fluid # 2: Dilute 5.7 mL glacial CH_3CH_2OOH with reagent water (See Section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 $\pm$ 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.8 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see Section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 7.1.4).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Section 7.1.3 to

determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20 °C until two successive weighing yield the same value within ± 1%. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet

the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 °C, and hold at 50 °C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100% solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the

solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (Sections 7.1.1 or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at

room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 7.2.12) or stored at 4 °C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains <0.5% dry solids (see Section 7.1.2), proceed to Section 7.2.13. If the waste contains >0.5% dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid

material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 °C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a

sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See Section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Section 4.6 are recommended for use under the conditions stated in Sections 4.6.1 - 4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid (see Section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains < 0.5% dry solids (Section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing $\geq$ 0.5% dry solids (Sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing < 5% solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing $\geq$ 5% solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 7.1.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 °C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace

slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see Section 7.1.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See Sections 7.3.13 through 7.3.15) or stored at 4 °C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following Sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 $\pm$ 2 °C during agitation.

7.3.13 Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the

TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Sections 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Section 7.3.13 and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 °C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.0 QUALITY ASSURANCE

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%Recovery) = 100\ (X_s - X_u)/K$$

where:
X_s = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and

150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentrations as the dependant variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES [DAYS]

	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Ruggedness. Two ruggedness studies have been performed to determine the effect of various perturbations on specific elements of the TCLP protocol. Ruggedness testing determines the sensitivity of small procedural variations which might be expected to occur during routine laboratory application.

9.1.1 Metals - The following conditions were used when leaching a waste for metals analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Extraction time	16 hours vs. 18 hours
Headspace	20% vs. 60%
Buffer #2 acidity	190 meq vs. 210 meq
Acid-washed filters	yes vs. no
Filter type	0.7 µm glass fiber vs. 0.45 µm vs. polycarbonate
Bottle type	borosilicate vs. flint glass

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom waste were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within $\pm$ 0.05 units as specified.

9.1.2 Volatile Organic Compounds - The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Headspace	0% vs. 5%
Buffer #1 acidity	60 meq vs. 80 meq
Method of storing extract	Syringe vs. Tedlar® bag
Aliquotting	yes vs. no
Pressure behind piston	0 psi vs. 20 psi

None of the parameters had a significant effect on the results of the ruggedness test.

9.2 Precision. Many TCLP precision (reproducibility) studies have been performed, and have shown that, in general, the precision of the TCLP is comparable to or exceeds that of the EP toxicity test and that method precision is adequate. One of the more significant contributions to poor precision appears to be related to sample homogeneity and inter-laboratory variation (due to the nature of waste materials).

9.2.1 Metals - The results of a multi-laboratory study are shown in Table 6, and indicate that a single analysis of a waste may not be adequate for waste characterization and identification requirements.

9.2.2 Semi-Volatile Organic Compounds - The results of two studies are shown in Tables 7 and 8. Single laboratory precision was excellent with greater than 90 percent of the results exhibiting an RSD less than 25 percent. Over 85 percent of all individual compounds in the multi-laboratory study fell in the RSD range of 20 - 120 percent. Both studies concluded that the TCLP provides adequate precision. It was also determined that the high acetate content of the extraction fluid did not present problems (i.e., column degradation of the gas chromatograph) for the analytical conditions used.

9.2.3 Volatile Organic Compounds - Eleven laboratories participated in a collaborative study of the use of the ZHE with two waste types which were fortified with a mixture of VOCs. The results of the collaborative study are shown in Table 9. Precision results for VOCs tend to occur over a considerable range. However, the range and mean RSD compared very closely to the same collaborative study metals results in Table 6. Blackburn and Show concluded that at the 95% level of significance: 1) recoveries among laboratories were statistically similar, 2) recoveries did not vary significantly between the two sample types, and 3) each laboratory showed the same pattern of recovery for each of the two samples.

10.0 REFERENCES

1. Blackburn, W.B. and Show, I. "Collaborative Study of the Toxicity Characteristics Leaching Procedure (TCLP)." Draft Final Report, Contract No. 68-03-1958, S-Cubed, November 1986.

2. Newcomer, L.R., Blackburn, W.B., Kimmell, T.A. "Performance of the Toxicity Characteristic Leaching Procedure." Wilson Laboratories, S-Cubed, U.S. EPA, December 1986.

3. Williams, L.R., Francis, C.W.; Maskarinec, M.P., Taylor D.R., and Rothman, N. "Single-Laboratory Evaluation of Mobility Procedure for Solid Waste." EMSL, ORNL, S-Cubed, ENSECO.

Table 1.
Volatile Analytes[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, and vinyl chloride are toxicity characteristic constituents.

Table 2.
Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S) 8-vessel extractor (DC20) 12-vessel extractor (DC20B) 24-vessel extractor (DC24C)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2-BRE) 4-vessel (3740-4-BRE) 6-vessel (3740-6-BRE) 8-vessel (3740-8-BRE) 12-vessel (3740-12-BRE) 24-vessel (3740-24-BRE)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE) 6-vessel (6VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 2-liter bottle extractor (YT310RAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

Table 3.
Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C1O2, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30O9OHW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device
Gelman Science	Ann Arbor, MI (800) 521-1520	15400 Gas Pressure Device

[1] Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4.
Suitable Filter Holders[1]

Company	Location	Model/ Catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5.
Suitable Filter Media[1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7
Gelman Science	Ann Arbor, MI (800) 521-1520	66256 (90mm) 66257 (142mm)	0.7

[1] Any filter that meets the specifications in Section 4.4 of the Method is suitable.

Table 6. Multi-Laboratory TCLP Metals, Precision

Waste	Extraction Fluid	Metal	$\bar{X}$	S	%RSD
Ammonia	#1	Cadmium	0.053	0.031	60
Lime Still	#2		0.023	0.017	76
Bottoms	#1	Chromium	0.015	0.0014	93
	#2		0.0032	0.0037	118
	#1	Lead	0.0030	0.0027	90
	#2		0.0032	0.0028	87
API/EW	#1	Cadmium	0.0046	0.0028	61
Mixture	#2		0.0005	0.0004	77
	#1	Chromium	0.0561	0.0227	40
	#2		0.105	0.018	17
	#1	Lead	0.0031	0.0031	100
	#2		0.0124	0.0136	110
Fossil	#1	Cadmium	0.080	0.069	86
Fuel Fly	#2		0.093	0.067	72
Ash	#1	Chromium	0.017	0.014	85
	#2		0.070	0.040	57
	#1	Lead	0.0087	0.0074	85
	#2		0.0457	0.0083	18
				%RSD Range = 17 - 118	
				Mean %RSD = 74	

NOTE: $\bar{X}$ = Mean results from 6 - 12 different laboratories
Units = mg/L
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 7. Single-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\bar{X}$	S	%RSD
Ammonia Lime Still Bottoms	Phenol	#1	19000	2230	11.6
		#2	19400	929	4.8
	2-Methylphenol	#1	2000	297	14.9
		#2	1860	52.9	2.8
	4-Methylphenol	#1	7940	1380	17.4
		#2	7490	200	2.7
	2,4-Dimethylphenol	#1	321	46.8	14.6
		#2	307	45.8	14.9
	Naphthalene	#1	3920	413	10.5
		#2	3827	176	4.6
	2-Methylnaphthalene	#1	290	44.8	15.5
		#2	273	19.3	7.1
	Dibenzofuran	#1	187	22.7	12.1
		#2	187	7.2	3.9
	Acenaphthylene	#1	703	89.2	12.7
		#2	663	20.1	3.0
	Fluorene	#1	151	17.6	11.7
		#2	156	2.1	1.3
	Phenanthrene	#1	241	22.7	9.4
		#2	243	7.9	3.3
	Anthracene	#1	33.2	6.19	18.6
		#2	34.6	1.55	4.5
	Fluoranthrene	#1	25.3	1.8	7.1
		#2	26.0	1.8	7.1
API/EW Mixture	Phenol	#1	40.7	13.5	33.0
		#2	19.0	1.76	9.3
	2,4-Dimethylphenol	#1	33.0	9.35	28.3
		#2	43.3	8.61	19.9
	Naphthalene	#1	185	29.4	15.8
		#2	165	24.8	15.0
	2-Methylnaphthalene	#1	265	61.2	23.1
		#2	200	18.9	9.5
					%RSD Range = 1 - 33
					Mean %RSD = 12

NOTE: Units = µg/L
Extractions were performed in triplicate
All results were at least 2x the detection limit
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 8. Multi-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\bar{X}$	S	%RSD
Ammonia Lime	BNAs	#1	10043	7680	76.5
Still Bottoms (A)		#2	10376	6552	63.1
API/EW	BNAs	#1	1624	675	41.6
Mixture (B)		#2	2074	1463	70.5
Fossil Fuel	BNAs	#1	750	175	23.4
Fly Ash (C)		#2	739	342	46.3
					Mean %RSD = 54

NOTE: Units = µg/L
X = Mean results from 3 - 10 labs
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

%RSD Range for Individual Compounds

A, #1	0 - 113
A, #2	28 - 108
B, #1	20 - 156
B, #2	49 - 128
C, #1	36 - 143
C, #2	61 - 164

Table 9. Multi-Laboratory (11 Labs) VOCs, Precision

Waste	Compound	$\bar{X}$	S	%RSD
Mine Tailings	Vinyl chloride	6.36	6.36	100
	Methylene chloride	12.1	11.8	98
	Carbon disulfide	5.57	2.83	51
	1,1-Dichloroethene	21.9	27.7	127
	1,1-Dichloroethane	31.4	25.4	81
	Chloroform	46.6	29.2	63
	1,2-Dichloroethane	47.8	33.6	70
	2-Butanone	43.5	36.9	85
	1,1,1-Trichloroethane	20.9	20.9	100
	Carbon tetrachloride	12.0	8.2	68
	Trichloroethene	24.7	21.2	86
	1,1,2-Trichloroethene	19.6	10.9	56
	Benzene	37.9	28.7	76
	1,1,2,2-Tetrachloroethane	34.9	25.6	73
	Toluene	29.3	11.2	38
	Chlorobenzene	35.6	19.3	54
	Ethylbenzene	4.27	2.80	66
	Trichlorofluoromethane	3.82	4.40	115
	Acrylonitrile	76.7	110.8	144
Ammonia Lime Still Bottoms	Vinyl chloride	5.00	4.71	94
	Methylene chloride	14.3	13.1	92
	Carbon disulfide	3.37	2.07	61
	1,1-Dichloroethene	52.1	38.8	75
	1,1-Dichloroethane	52.8	25.6	49
	Chloroform	64.7	28.4	44
	1,2-Dichloroethane	43.1	31.5	73
	2-Butanone	59.0	39.6	67
	1,1,1-Trichloroethane	53.6	40.9	76
	Carbon tetrachloride	7.10	6.1	86
	Trichloroethene	57.3	34.2	60
	1,1,2-Trichloroethene	6.7	4.7	70
	Benzene	61.3	26.8	44
	1,1,2,2-Tetrachloroethane	3.16	2.1	66
	Toluene	69.0	18.5	27
	Chlorobenzene	71.8	12.0	17
	Ethylbenzene	3.70	2.2	58
	Trichlorofluoromethane	4.05	4.8	119
	Acrylonitrile	29.4	34.8	118
				%RSD Range = 17 - 144 Mean %RSD = 75

NOTE: Units = µg/L

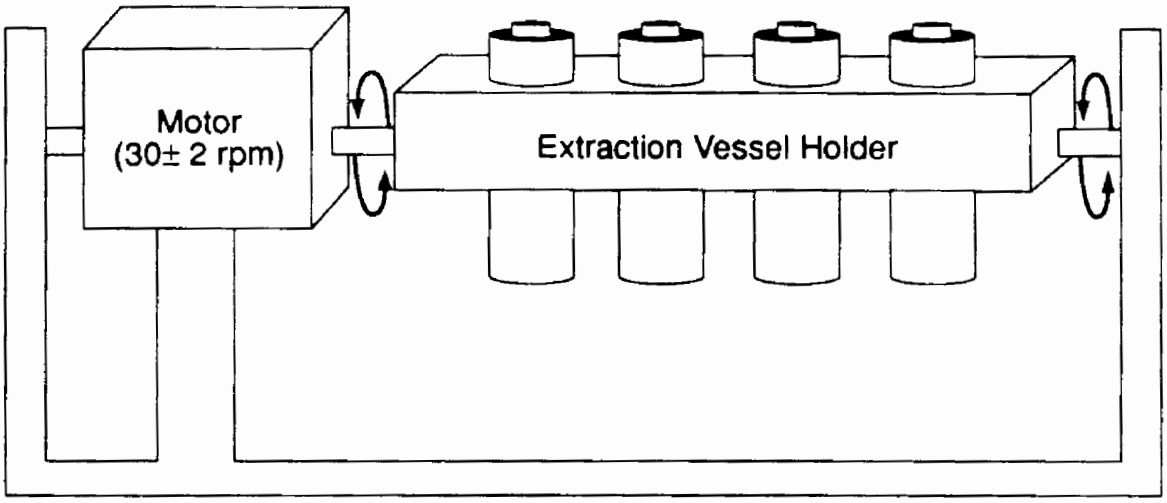


Figure 1. Rotary Agitation Apparatus

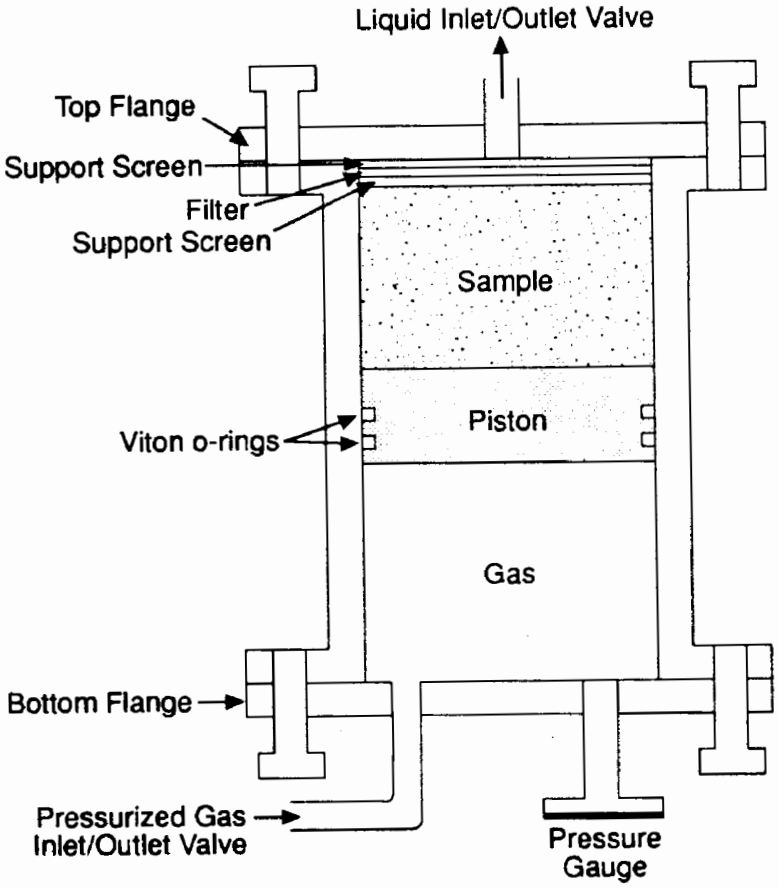
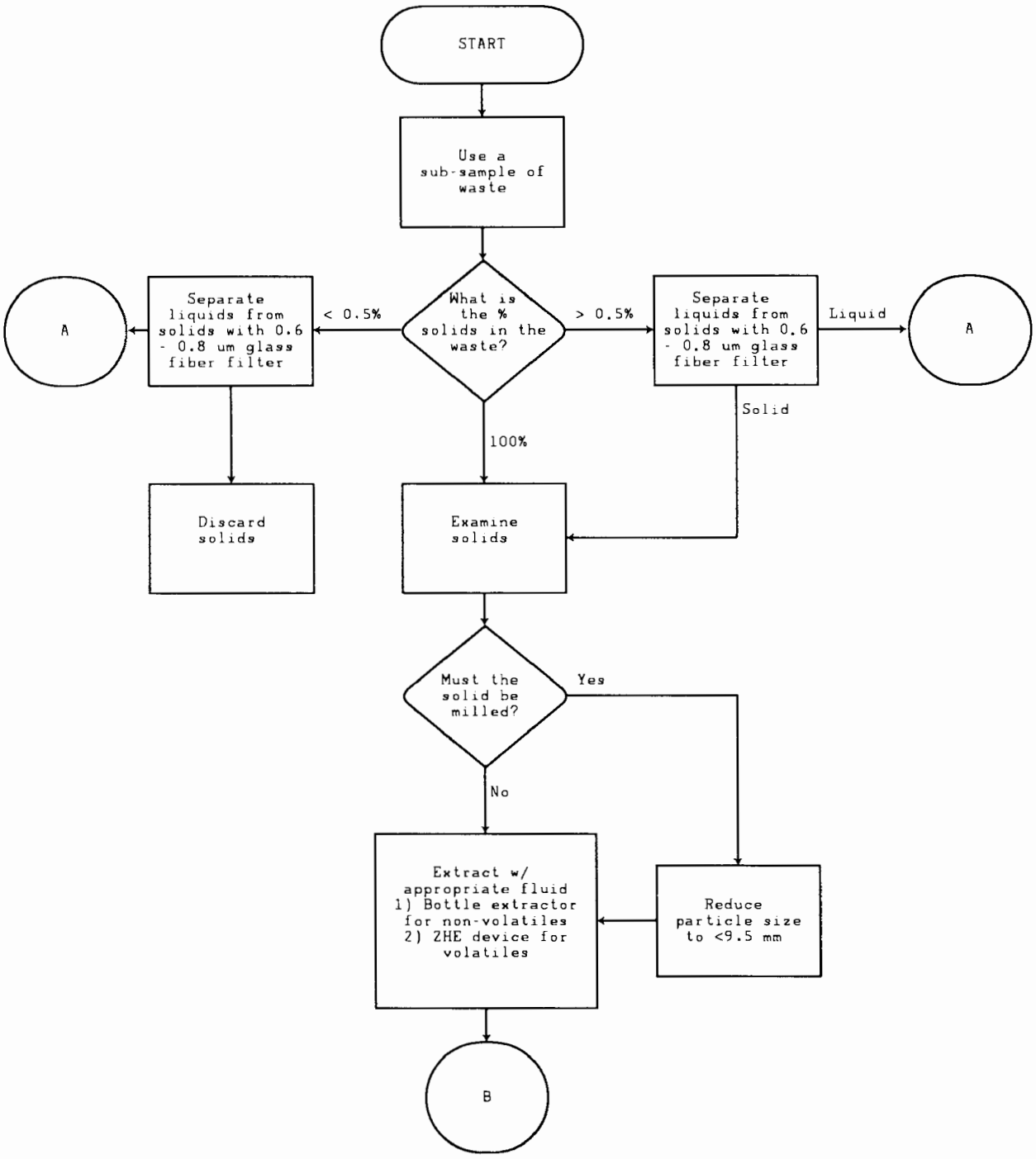
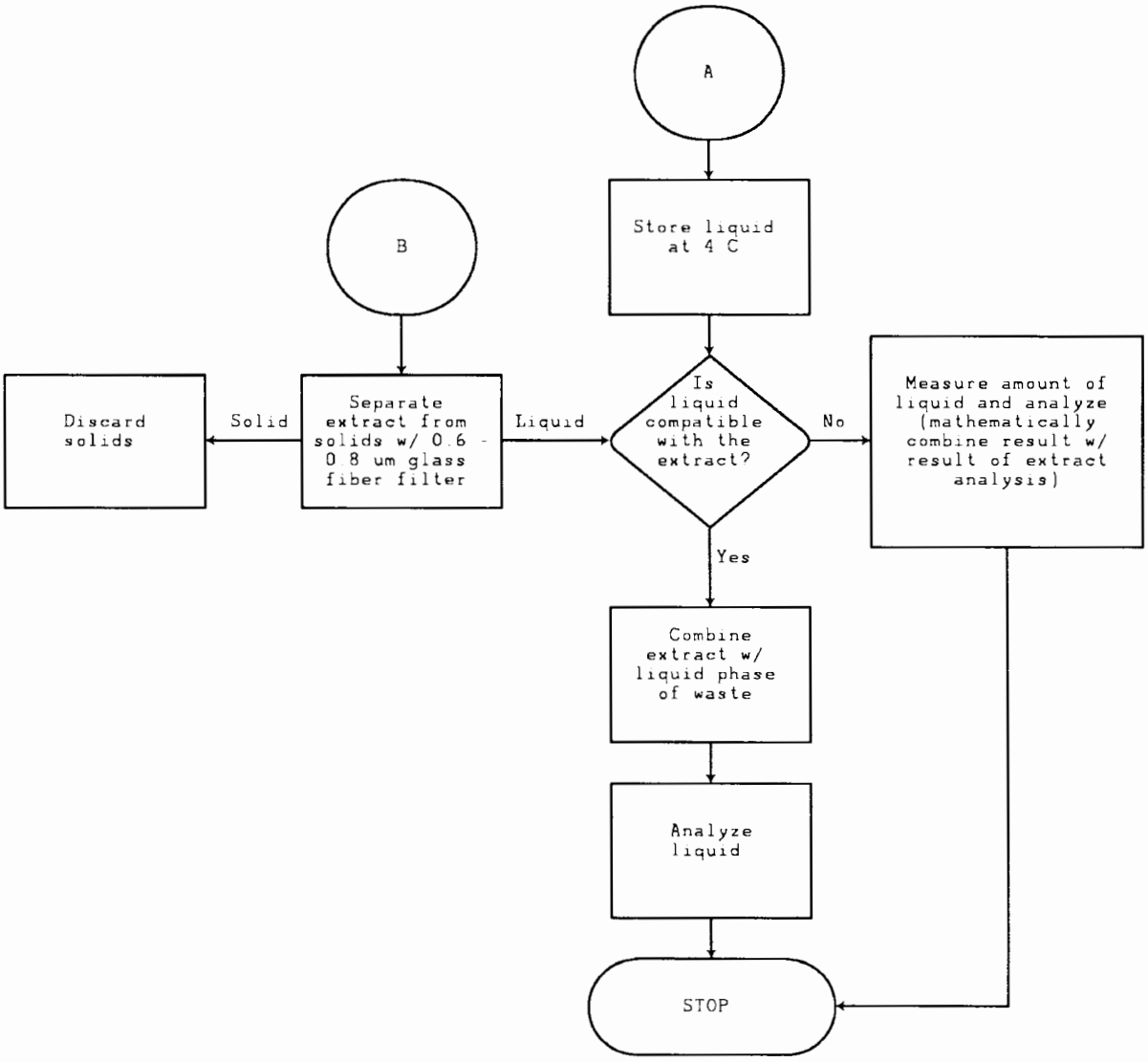


Figure 2. Zero-Headspace Extractor (ZHE)

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes.

2.0 SUMMARY OF METHOD

2.1 For liquid samples (i.e., those containing less than 0.5 % dry solid material), the sample, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the 1312 extract.

2.2 For samples containing greater than 0.5 % solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero Headspace Extraction Vessel (ZHE). This device is for use only when the sample is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device and effectively precludes headspace. This type of vessel allows for initial liquid/solid

separation, extraction, and final extract filtration without opening the vessel (see Step 4.3.1). These vessels shall have an internal volume of 500-600 mL and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psig or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for 1312 analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psig, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psig, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Step 7.3) refers to pounds-per-square-inch (psig), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the sample is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extraction Vessel (ZHE): When the sample is evaluated for volatiles, the zero-headspace extraction vessel described

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[1]VITON® is a trademark of Du Pont.

in Step 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psig).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the sample is evaluated for other than volatile analytes, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psig or more. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10 %) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are listed in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb sample components of interest. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8-μm . Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with reagent water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to $\pm$ 0.05 units at 25°C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract when using the ZHE device. These devices listed are recommended for use under the following conditions:

[2]TEDLAR® is a registered trademark of Du Pont.

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1 % of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1 % of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 % solid) or has no significant solid phase (is <0.5% solid) , either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas-tight syringe, pressure filtration unit (see Step 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 ± 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Sulfuric acid/nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid. If preferred, a more dilute H_2SO_4/HNO_3 acid mixture may be prepared and used in steps 5.4.1 and 5.4.2 making it easier to adjust the pH of the extraction fluids.

5.4 Extraction fluids.

5.4.1 Extraction fluid #1: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 4.20 ± 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained.

5.4.2 Extraction fluid #2: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 5.00 ± 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

5.4.3 Extraction fluid #3: This fluid is reagent water (Step 5.2) and is used to determine cyanide and volatiles leachability.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.5 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 There may be requirements on the minimal size of the field sample depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for the preliminary evaluations of the percent

solids and the particle size. An aliquot may be needed to conduct the nonvolatile analyte extraction procedure. If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the sample is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4°C. Samples should be opened only immediately prior to extraction).

6.6 1312 extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Step 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Step 8.0 (Quality Control) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary 1312 evaluations on a minimum 100 gram aliquot of sample. This aliquot may not actually undergo 1312 extraction. These preliminary evaluations include: (1) determination of the percent solids (Step 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Step 7.1.2); and (3) determination of whether the solid portion of the waste requires particle size reduction (Step 7.1.3).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the sample will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solid), weigh out a representative subsample (100 g minimum) and proceed to Step 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device

discussed in Step 4.3.2, and is outlined in Steps 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Gradually apply vacuum or gentle pressure of 1-10 psig, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psig, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psig increments to a maximum of 50 psig. After each incremental increase of 10 psig, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psig (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration.

NOTE: If sample material (>1 % of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.1.5 to determine the weight of the sample that will be filtered.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid, but even after applying vacuum or pressure filtration, as outlined in Step 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the sample by subtracting the weight of the liquid phase from the weight of the total sample, as determined in Step 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Step 7.1.1.9)}}{\text{Total weight of waste (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Step 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Step 7.1.3 to determine whether the solid material requires particle size reduction or to Step 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Step 7.1.1.9 is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 with a fresh portion of the waste if the volatile 1312 analysis is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 $\pm$ 20°C until two successive weighings yield the same value within $\pm$ 1 %. Record the final weight.

Caution: The drying oven should be vented to a hood or other appropriate device to eliminate the possibility of fumes from the sample escaping into the laboratory. Care should be taken to ensure that the sample will not flash or violently react upon heating.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Weight of dry sample + filter) - tared weight of filter}}{\text{Initial weight of sample (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 if the volatile 1312 analysis is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile 1312 analysis is to be performed, return to the beginning of this Step (7.1) and, with a fresh portion of sample, determine whether particle size reduction is necessary (Step 7.1.3).

7.1.3 Determination of whether the sample requires particle-size reduction (particle-size is reduced during this step): Using the solid portion of the sample, evaluate the solid for particle size. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Step 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid:

7.1.4.1 For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 should be used.

7.1.4.2 For wastes and wastewater, extraction fluid #1 should be used.

7.1.4.3 For cyanide-containing wastes and/or soils, extraction fluid #3 (reagent water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.1.5 If the aliquot of the sample used for the preliminary evaluation (Steps 7.1.1 - 7.1.4) was determined to be 100% solid at Step 7.1.1.1, then it can be used for the Step 7.2 extraction (assuming at least 100 grams remain), and the Step 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Step 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Step 7.3. The aliquot of the waste subjected to the procedure in Step 7.1.1.7 might be appropriate for use for the Step 7.2 extraction if an adequate amount of solid (as determined by Step 7.1.1.9)

was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Step 7.2.10 of the nonvolatile 1312 extraction.

7.2 Procedure When Volatiles Are Not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of 1312 extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single 1312 extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 % solid, see Step 7.1.1), weigh out a subsample of the sample (100 gram minimum) and proceed to Step 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Step 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the sample (100 gram minimum) and record the weight. If the waste contains <0.5 % dry solids (Step 7.1.2), the liquid portion of the waste, after filtration, is defined as the 1312 extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the 1312 extract. For wastes containing >0.5 % dry solids (Steps 7.1.1 or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the 1312 extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered followed by

filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the sample (liquid and solid phases) to the filter holder (see Step 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Gradually apply vacuum or gentle pressure of 1-10 psig, until air or pressurizing gas moves through the filter. If this point if not reached under 10 psig, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psig increments to maximum of 50 psig. After each incremental increase of 10 psig, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psig (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

NOTE: If waste material (>1 % of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.2.5, to determine the weight of the waste sample that will be filtered.

NOTE:Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Step 7.2.12) or stored at 4°C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the sample contains <0.5% dry solids (see Step 7.1.2), proceed to Step 7.2.13. If the sample contains >0.5 % dry solids (see Step 7.1.1 or 7.1.2), and if particle-size reduction of the solid was needed in Step 7.1.3, proceed to Step 7.2.10. If the sample as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 7.2.11.

7.2.10 Prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described in Step 7.1.3. When the surface area or particle-size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \%\ \text{solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Step 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary extractor device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2°C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of sample (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 7.2.7. For final filtration of the 1312 extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Step 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the 1312 extract as follows:

7.2.13.1 If the sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.2.12 is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Step 7.2.12 with the initial liquid phase of the sample obtained

in Step 7.2.7. This combined liquid is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Step 7.2.7, is not or may not be compatible with the filtered liquid resulting from Step 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the 1312 extract, and combine the results mathematically, as described in Step 7.2.14.

7.2.14 Following collection of the 1312 extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH < 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The 1312 extract shall be prepared and analyzed according to appropriate analytical methods. 1312 extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5 %), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\,(C_1) + (V_2)\,(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles Are Involved

Use the ZHE device to obtain 1312 extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psig), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (see Step 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Step 4.6 are recommended for use under the conditions stated in Steps 4.6.1-4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Step 7.3, Step 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the sample is 100% solid (see Step 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Step 7.3.5.

7.3.4 If the sample contains <0.5% dry solids (Step 7.1.2), the liquid portion of waste, after filtration, is defined as the 1312 extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For samples containing $\geq$0.5% dry solids (Steps 7.1.1 and/or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For samples containing <5% solids (see Step 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing >5% solids (see Step 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Step 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle-size reduction of the solid portion of the sample was required in Step 7.1.3, proceed to Step 7.3.6. If particle-size reduction was not required in Step 7.1.3, proceed to Step 7.3.7.

7.3.6 Prepare the sample for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Step 7.1.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle-size reduction. The means used to effect particle-size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge samples prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens into the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extraction collection device to the top plate.

Note: If sample material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psig (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4°C reduces the

amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 % solid (see Step 7.1.1), slowly increase the pressure to a maximum of 50 psig to force most of the headspace out of the device and proceed to Step 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psig to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psig increments to a maximum of 50 psig. After each incremental increase of 10 psig, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When liquid flow has ceased such that continued pressure filtration at 50 psig does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the 1312 extraction as a solid.

If the original waste contained <0.5 % dry solids (see Step 7.1.2), this filtrate is defined as the 1312 extract and is analyzed directly. Proceed to Step 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (see Steps 7.3.13 through 7.3.15) or stored at 4°C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #3 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \%\ \text{solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #3 is used in all cases (see Step 5.4.3).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psig (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psig and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary extractor apparatus (if it is not already there) and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 $\pm$ 2°C during agitation.

7.3.13 Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the ZHE is leaking. Check the ZHE for leaking as specified in Step 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Step 7.3.9. All extracts shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Steps 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured

7.3.14 If the original sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.3.13 is defined as the 1312 extract. If the sample contained an initial liquid phase, the filtered liquid material obtained from Step 7.3.13 and the initial liquid phase (Step 7.3.9) are collectively defined as the 1312 extract.

7.3.15 Following collection of the 1312 extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C until analyzed. Analyze the 1312 extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume- weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\,(C_1) + (V_2)\,(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Step 8.0 for quality assurance requirements.

8.0 QUALITY CONTROL

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) for every 20 extractions that have been conducted in an extraction vessel. Refer to Chapter One for additional quality control protocols.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the 1312 extract and before preservation. Matrix spikes should not be added prior to 1312 extraction of the sample.

8.2.2 In most cases, matrix spike levels should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the

spike concentration may be as low as one half of the analyte concentration, but may not be less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of 1312 extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the 1312 extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%\ \text{Recovery}) = 100\ (X_s - X_u) / K$$

where:

X_s = measured value for the spiked sample
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the 1312 extract is not at least 50% and the concentration does not exceed the appropriate regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standards as the independent variable (x-axis). Solve for the intercept

of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentrations as the dependant variable versus the independent variable. Derive concentrations for the unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo 1312 extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES (days)

	From: Field Collection To: 1312 extraction	From: 1312 extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total Elapsed Time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360
NA = Not Applicable				

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Precision results for semi-volatiles and metals: An eastern soil with high organic content and a western soil with low organic content were used for the semi-volatile and metal leaching experiments. Both types of soil were analyzed prior to contaminant spiking. The results are shown in Table 6. The concentration of contaminants leached from the soils were reproducible, as shown

by the moderate relative standard deviations (RSDs) of the recoveries (averaging 29% for the compounds and elements analyzed).

9.2 Precision results for volatiles: Four different soils were spiked and tested for the extraction of volatiles. Soils One and Two were from western and eastern Superfund sites. Soils Three and Four were mixtures of a western soil with low organic content and two different municipal sludges. The results are shown in Table 7. Extract concentrations of volatile organics from the eastern soil were lower than from the western soil. Replicate leachings of Soils Three and Four showed lower precision than the leachates from the Superfund soils.

10.0 REFERENCES

1. Environmental Monitoring Systems Laboratory, "Performance Testing of Method 1312; QA Support for RCRA Testing: Project Report". EPA/600/4-89/022. EPA Contract 68-03-3249 to Lockheed Engineering and Sciences Company, June 1989.

2. Research Triangle Institute, "Interlaboratory Comparison of Methods 1310, 1311, and 1312 for Lead in Soil". U.S. EPA Contract 68-01-7075, November 1988.

Table 1. Volatile Analytes[1]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

Table 2. Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S); 8-vessel extractor (DC20); 12-vessel extractor (DC20B)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2); 4-vessel (3740-4); 6-vessel (3740-6); 8-vessel (3740-8); 12-vessel (3740-12); 24-vessel (3740-24)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 1-liter bottle extractor (YT300RAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ±2 rpm is acceptable.

Table 3. Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C1O2, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT3OO9OHW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device

[1] Any device that meets the specifications listed in Step 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4. Suitable Filter Holders[1]

Company	Location	Model/ Catalogue #	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5. Suitable Filter Media[1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7

[1] Any filter that meets the specifications in Step 4.4 of the Method is suitable.

TABLE 6 - METHOD 1312 PRECISION RESULTS FOR SEMI-VOLATILES AND METALS

		Eastern Soil (pH 4.2)		Western Soil (pH 5.0)	
	Amount Spiked (µg)	Amount Recovered* (µg)	% RSD	Amount Recovered* (µg)	% RSD
FORTIFIED ANALYTES					
bis(2-chloroethyl)-ether	1040	834	12.5	616	14.2
2-Chlorophenol	1620	1010	6.8	525	54.9
1,4-Dichlorobenzene	2000	344	12.3	272	34.6
1,2-Dichlorobenzene	8920	1010	8.0	1520	28.4
2-Methylphenol	3940	1860	7.7	1130	32.6
Nitrobenzene	1010	812	10.0	457	21.3
2,4-Dimethylphenol	1460	200	18.4	18	87.6
Hexachlorobutadiene	6300	95	12.9	280	22.8
Acenaphthene	3640	210	8.1	310**	7.7
2,4-Dinitrophenol	1300	896**	6.1	23**	15.7
2,4-Dinitrotoluene	1900	1150	5.4	585	54.4
Hexachlorobenzene	1840	3.7	12.0	10	173.2
gamma BHC (Lindane)	7440	230	16.3	1240	55.2
beta BHC	640	35	13.3	65.3	51.7
METALS					
Lead	5000	70	4.3	10	51.7
Cadmium	1000	387	2.3	91	71.3

* = Triplicate analyses.
** = Duplicate analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.

TABLE 7 - METHOD 1312 PRECISION RESULTS FOR VOLATILES

Compound Name	Soil No. 1 (Western) Avg. %Rec.*	%RSD	Soil No. 2 (Eastern) Avg. %Rec.*	%RSD	Soil No. 3 (Western and Sludge) Avg. %Rec.**	%RSD	Soil No. 4 (Western and Sludge) Avg. %Rec.***	%RSD
Acetone	44.0	12.4	43.8	2.25	116.0	11.5	21.3	71.4
Acrylonitrile	52.5	68.4	50.5	70.0	49.3	44.9	51.8	4.6
Benzene	47.8	8.29	34.8	16.3	49.8	36.7	33.4	41.1
n-Butyl Alcohol (1-Butanol)	55.5	2.91	49.2	14.6	65.5	37.2	73.0	13.9
Carbon disulfide	21.4	16.4	12.9	49.5	36.5	51.5	21.3	31.5
Carbon tetrachloride	40.6	18.6	22.3	29.1	36.2	41.4	24.0	34.0
Chlorobenzene	64.4	6.76	41.5	13.1	44.2	32.0	33.0	24.9
Chloroform	61.3	8.04	54.8	16.4	61.8	29.1	45.8	38.6
1,2-Dichloroethane	73.4	4.59	68.7	11.3	58.3	33.3	41.2	37.8
1,1-Dichloroethane	31.4	14.5	22.9	39.3	32.0	54.4	16.8	26.4
Ethyl acetate	76.4	9.65	75.4	4.02	23.0	119.8	11.0	115.5
Ethylbenzene	56.2	9.22	23.2	11.5	37.5	36.1	27.2	28.6
Ethyl ether	48.0	16.4	55.1	9.72	37.3	31.2	42.0	17.6
Isobutanol (4-Methyl -1-propanol)	0.0	ND	0.0	ND	61.8	37.7	76.0	12.2
Methylene chloride	47.5	30.3	42.2	42.9	52.0	37.4	37.3	16.6
Methyl ethyl ketone (2-Butanone)	56.7	5.94	61.9	3.94	73.7	31.3	40.6	39.0
Methyl isobutyl ketone	81.1	10.3	88.9	2.99	58.3	32.6	39.8	40.3
1,1,1,2-Tetrachloroethane	69.0	6.73	41.1	11.3	50.8	31.5	36.8	23.8
1,1,2,2-Tetrachloroethane	85.3	7.04	58.9	4.15	64.0	25.7	53.6	15.8
Tetrachloroethene	45.1	12.7	15.2	17.4	26.2	44.0	18.6	24.2
Toluene	59.2	8.06	49.3	10.5	45.7	35.2	31.4	37.2
1,1,1-Trichloroethane	47.2	16.0	33.8	22.8	40.7	40.6	26.2	38.8
1,1,2-Trichloroethane	76.2	5.72	67.3	8.43	61.7	28.0	46.4	25.4
Trichloroethene	54.5	11.1	39.4	19.5	38.8	40.9	25.6	34.1
Trichlorofluoromethane	20.7	24.5	12.6	60.1	28.5	34.0	19.8	33.9
1,1,2-Trichlorotrifluoroethane	18.1	26.7	6.95	58.0	21.5	67.8	15.3	24.8
Vinyl chloride	10.2	20.3	7.17	72.8	25.0	61.0	11.8	25.4

* Triplicate analyses
** Six replicate analyses
*** Five replicate analyses

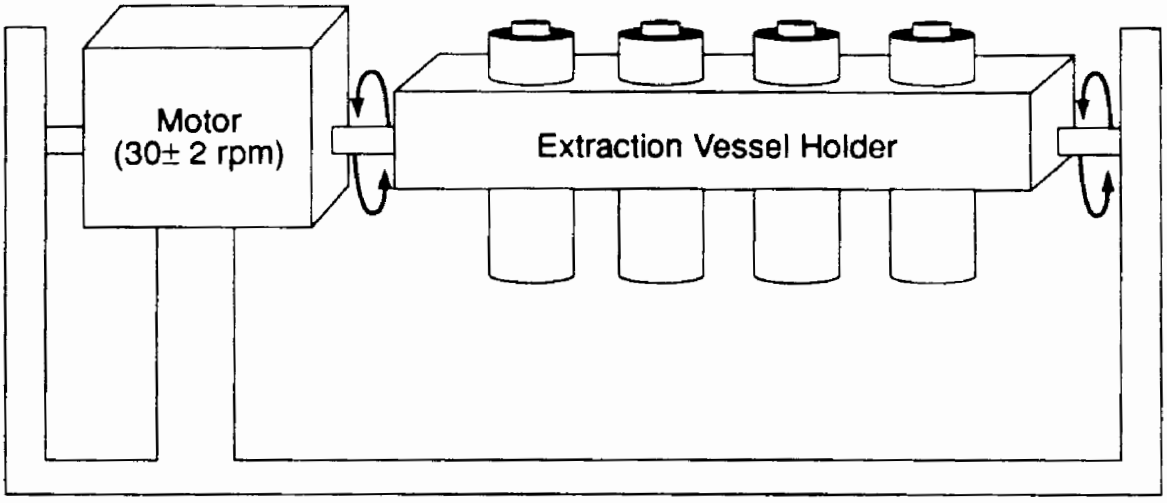


Figure 1. Rotary Agitation Apparatus

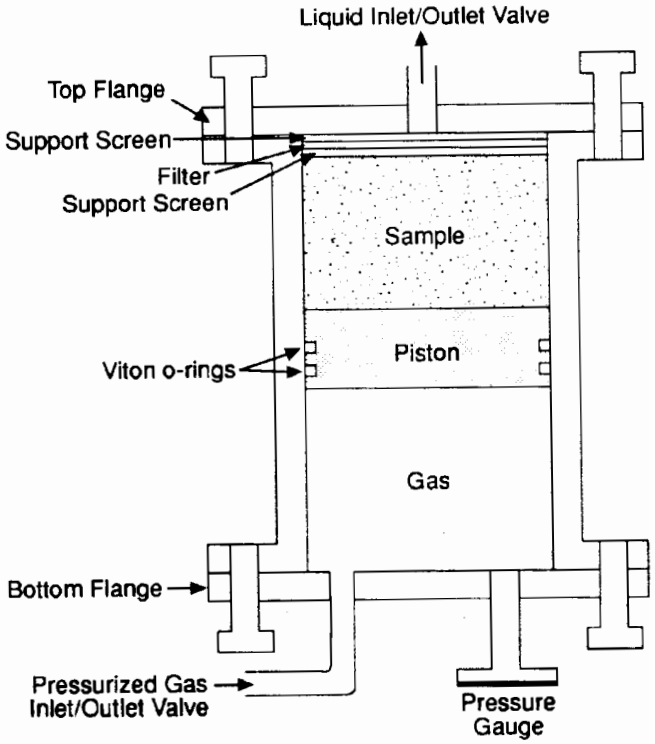
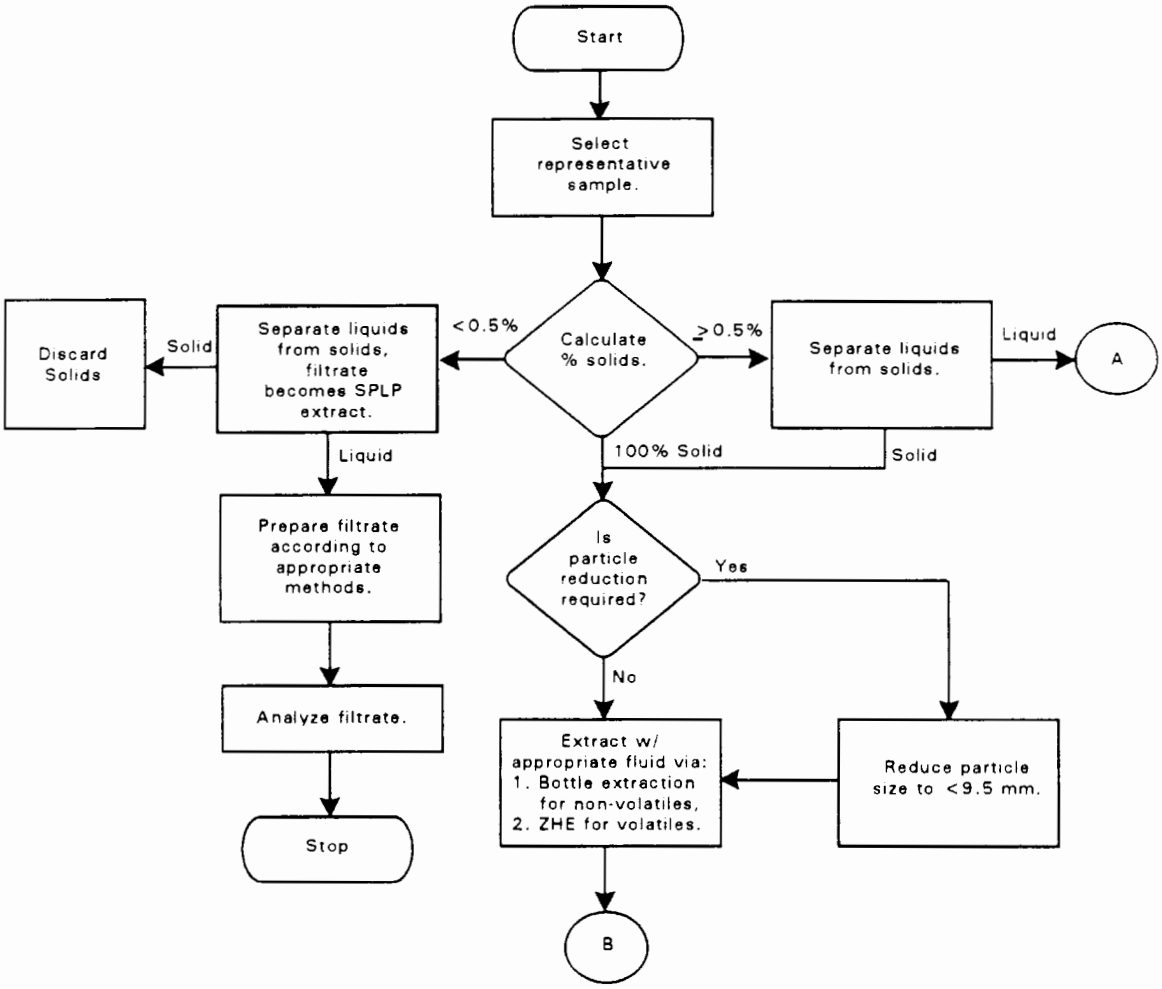
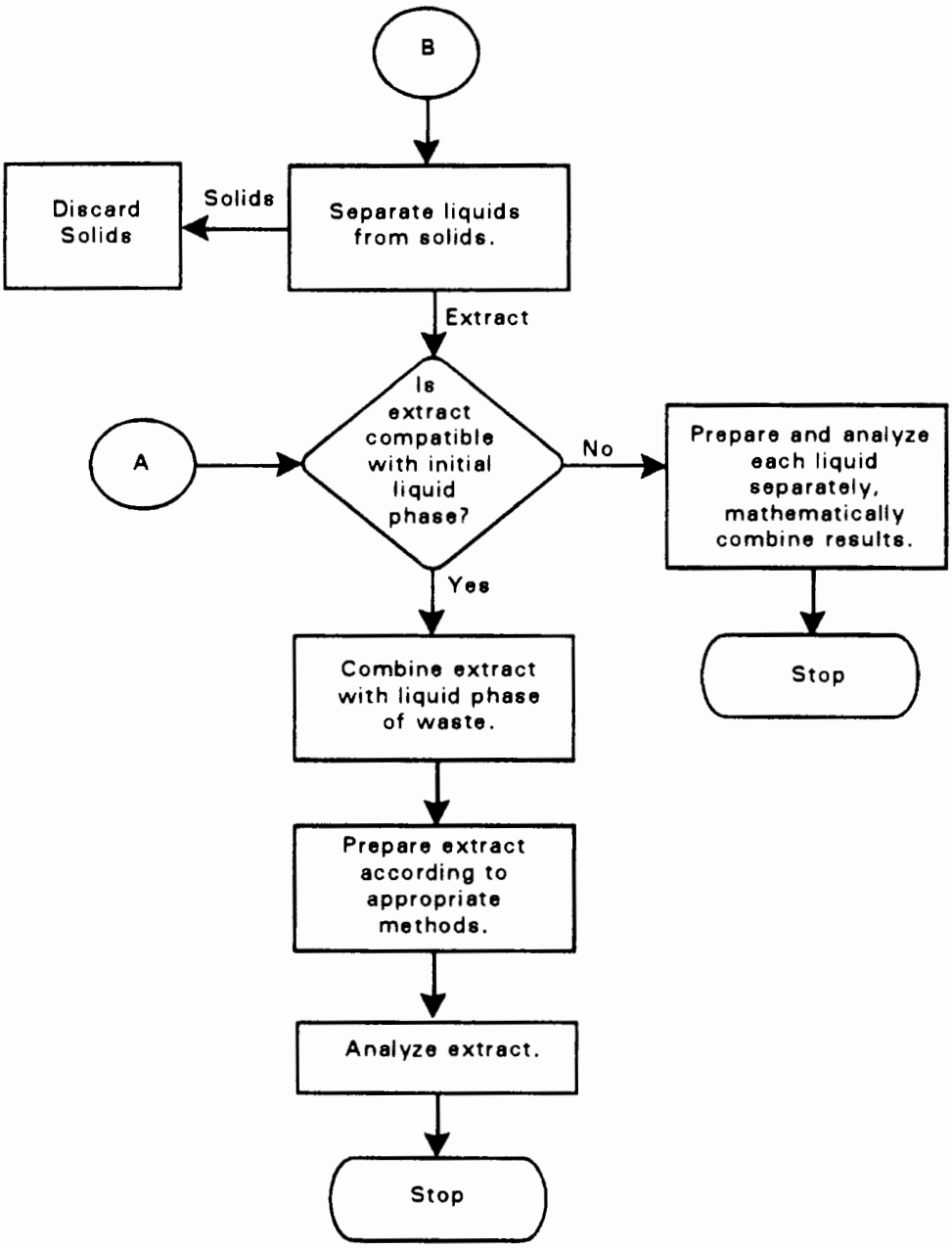


Figure 2. Zero-Headspace Extractor (ZHE)

SYNTHETIC PRECIPITATION LEACHING PROCEDURE




B
Separate liquids from solids.
Solids
Discard Solids
Extract
A
Is extract compatible with initial liquid phase?
No
Prepare and analyze each liquid separately, mathematically combine results.
Stop
Yes
Combine extract with liquid phase of waste.
Prepare extract according to appropriate methods.
Analyze extract.
Stop

MULTIPLE EXTRACTION PROCEDURE

1.0 SCOPE AND APPLICATION

The Multiple Extraction Procedure (MEP) described in this method is designed to simulate the leaching that a waste will undergo from repetitive precipitation of acid rain on an improperly designed sanitary landfill. The repetitive extractions reveal the highest concentration of each constituent that is likely to leach in a natural environment. Method 1320 is applicable to liquid, solid, and multiphase samples.

2.0 SUMMARY OF METHOD

Waste samples are extracted according to the Extraction Procedure Toxicity Test (Method 1310, Chapter 8) and analyzed for the constituents of concern listed in Chapter 7, Table 7-1: Maximum Concentration of Contaminants for Characteristic of EP Toxicity, using the 7000 and 8000 series methods. Then the solid portions of the samples that remain after application of Method 1310 are re-extracted nine times using synthetic acid rain extraction fluid. If the concentration of any constituent of concern increases from the 7th or 8th extraction to the 9th extraction, the procedure is repeated until these concentrations decrease.

3.0 INTERFERENCES

Potential interferences that may be encountered during analysis are discussed in the appropriate analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Refer to Method 1310.

5.0 REAGENTS

5.1 Refer to Method 1310.

5.2 Sulfuric acid:nitric acid, 60/40 weight percent mixture: Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 1310.

7.0 PROCEDURE

7.1 Run the Extraction Procedure (EP) test in Method 1310.

7.2 Analyze the extract for the constituents of interest.

7.3 Prepare a synthetic acid rain extraction fluid by adding the 60/40 weight percent sulfuric acid and nitric acid to distilled deionized water until the pH is 3.0 $\pm$ 0.2.

7.4 Take the solid phase of the sample remaining after the Separation Procedure of the Extraction Procedure and weigh it. Measure an aliquot of synthetic acid rain extraction fluid equal to 20 times the weight of the solid sample. Do not allow the solid sample to dry before weighing.

7.5 Combine the solid phase sample and acid rain fluid in the same extractor as used in the EP and begin agitation. Record the pH within 5-10 min after agitation has been started.

7.6 Agitate the mixture for 24 hr, maintaining the temperature at 20-40°C (68-104°F). Record the pH at the end of the 24-hr extraction period.

7.7 Repeat the Separation Procedure as described in Method 1310.

7.8 Analyze the extract for the constituents of concern.

7.9 Repeat steps 7.4-7.8 eight additional times.

7.10 If, after completing the ninth synthetic rain extraction, the concentration of any of the constituents of concern is increasing over that found in the 7th and 8th extractions, then continue extracting with synthetic acid rain until the concentration in the extract ceases to increase.

7.11 Report the initial and final pH of each extraction and the concentration of each listed constituent of concern in each extract.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 All quality control measures suggested in the referenced analytical methods should be followed.

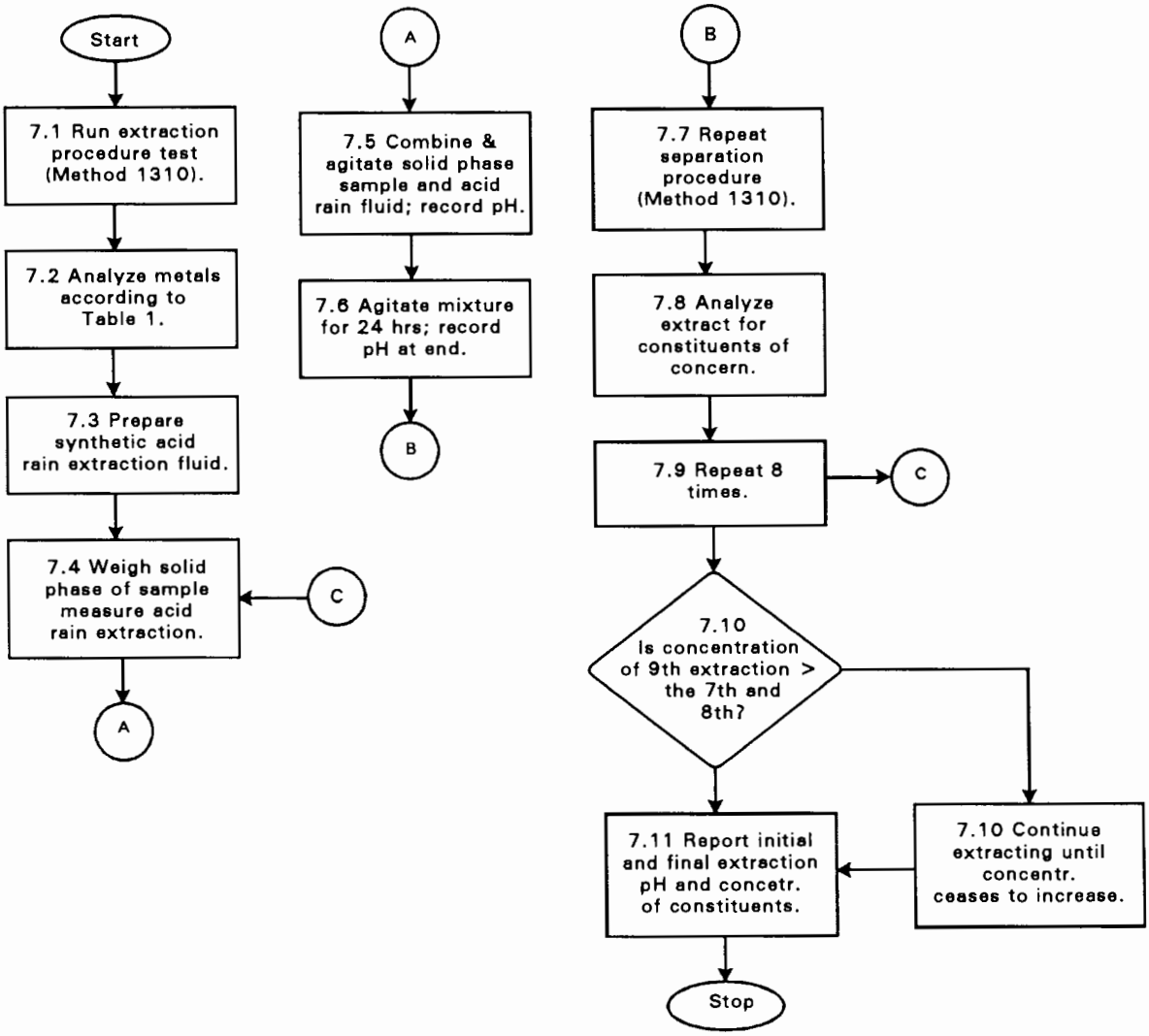
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 1320
MULTIPLE EXTRACTION PROCEDURE



METHOD 1330A

EXTRACTION PROCEDURE FOR OILY WASTES

1.0 SCOPE AND APPLICATION

1.1 Method 1330 is used to determine the mobile metal concentration (MMC) in oily wastes.

1.2 Method 1330 is applicable to API separator sludges, rag oils, slop oil emulsions, and other oil wastes derived from petroleum refining.

2.0 SUMMARY OF METHOD

2.1 The sample is separated into solid and liquid components by filtration.

2.2 The solid phase is placed in a Soxhlet extractor, charged with tetrahydrofuran, and extracted. The THF is removed, the extractor is then charged with toluene, and the sample is reextracted.

2.3 The EP method (Method 1310) is run on the dry solid residue.

2.4 The original liquid, combined extracts, and EP leachate are analyzed for the EP metals.

3.0 INTERFERENCES

3.1 Matrix interferences will be coextracted from the sample. The extent of these interferences will vary considerably from waste to waste, depending on the nature and diversity of the particular refinery waste being analyzed.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extraction apparatus.

4.2 Vacuum pump or other source of vacuum.

4.3 Buchner funnel 12.

4.4 Electric heating mantle.

4.5 Paper extraction thimble.

4.6 Filter paper.

4.7 Muslin cloth disks.

4.8 Evaporative flask - 250-mL.

4.9 Balance - Analytical, capable of weighing to $\pm$ 0.5 mg.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Tetrahydrofuran, C_4H_8O.

5.4 Toluene, $C_6H_5CH_3$.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples must be collected in glass containers having a total volume of at least 150 mL. No solid material should interfere with sealing the sample container.

6.2 Sampling devices should be wiped clean with paper towels or absorbent cloth, rinsed with a small amount of hexane followed by acetone rinse, and dried between samples. Alternatively, samples can be taken with disposable sampling devices in beakers.

7.0 PROCEDURE

7.1 Separate the sample (minimum 100 g) into its solid and liquid components. The liquid component is defined as that portion of the sample which passes through a 0.45 µm filter media under a pressure differential of 75 psi.

7.2 Determine the quantity of liquid (mL) and the concentration of the toxicants of concern in the liquid phase (mg/L).

7.3 Place the solid phase into a Soxhlet extractor, charge the concentration flask with 300 mL tetrahydrofuran, and extract for 3 hours.

7.4 Remove the flask containing tetrahydrofuran and replace it with one containing 300 mL toluene.

7.5 Extract the solid a second time, for 3 hours, with the toluene.

7.6 Combine the tetrahydrofuran and toluene extracts.

7.7 Analyze the combined extracts for the toxicants of concern.

7.8 Determine the quantity of liquid (mL) and the concentration of the toxicants of concern in the combined extracts (mg/L).

7.9 Take the solid material remaining in the Soxhlet thimble and dry it at 100°C for 30 minutes.

7.10 Run the EP (Method 1310) on the dried solid.

7.11 Calculate the mobile metal concentration (MMC) in mg/L using the following formula:

$$MMC = 1{,}000 \times \frac{(Q_1 + Q_2 + Q_3)}{(L_1 + L_2 + L_3)}$$

where:

Q_1 = Mass of toxicant in initial liquid phase of sample (amount of liquid x concentration of toxicant) (mg).

Q_2 = Mass of toxicant in combined organic extracts of sample (amount of liquid x concentration of toxicant) (mg).

Q_3 = Mass of toxicant in EP extract of solid (amount of extract x concentration of toxicant) (mg).

L_1 = Volume of initial liquid (mL).

L_2 = Volume of liquid in THF and toluene extract (Step 7.8) (mL).

L_3 = Volume of liquid in EP (mL) = 20 x [weight of dried solid from Step 7.9 (g)].

8.0 QUALITY CONTROL

8.1 Any reagent blanks or replicates samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

Figure 1. Extractor

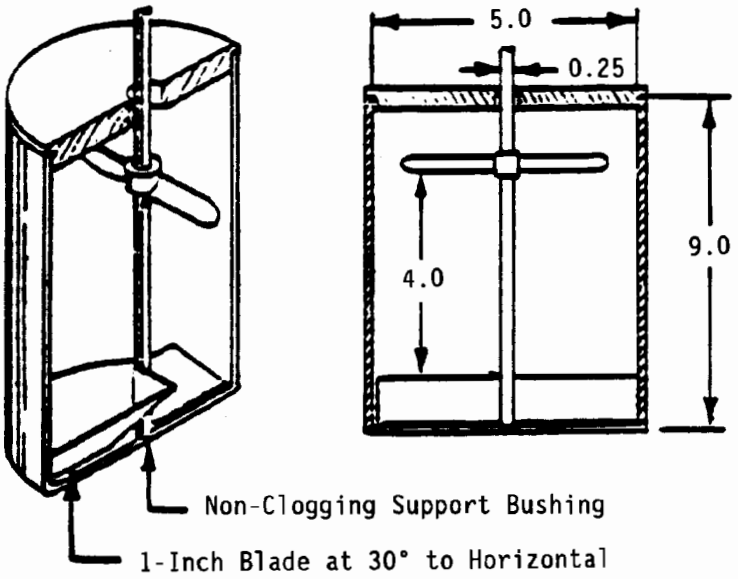


Figure 2. Rotary Extractor

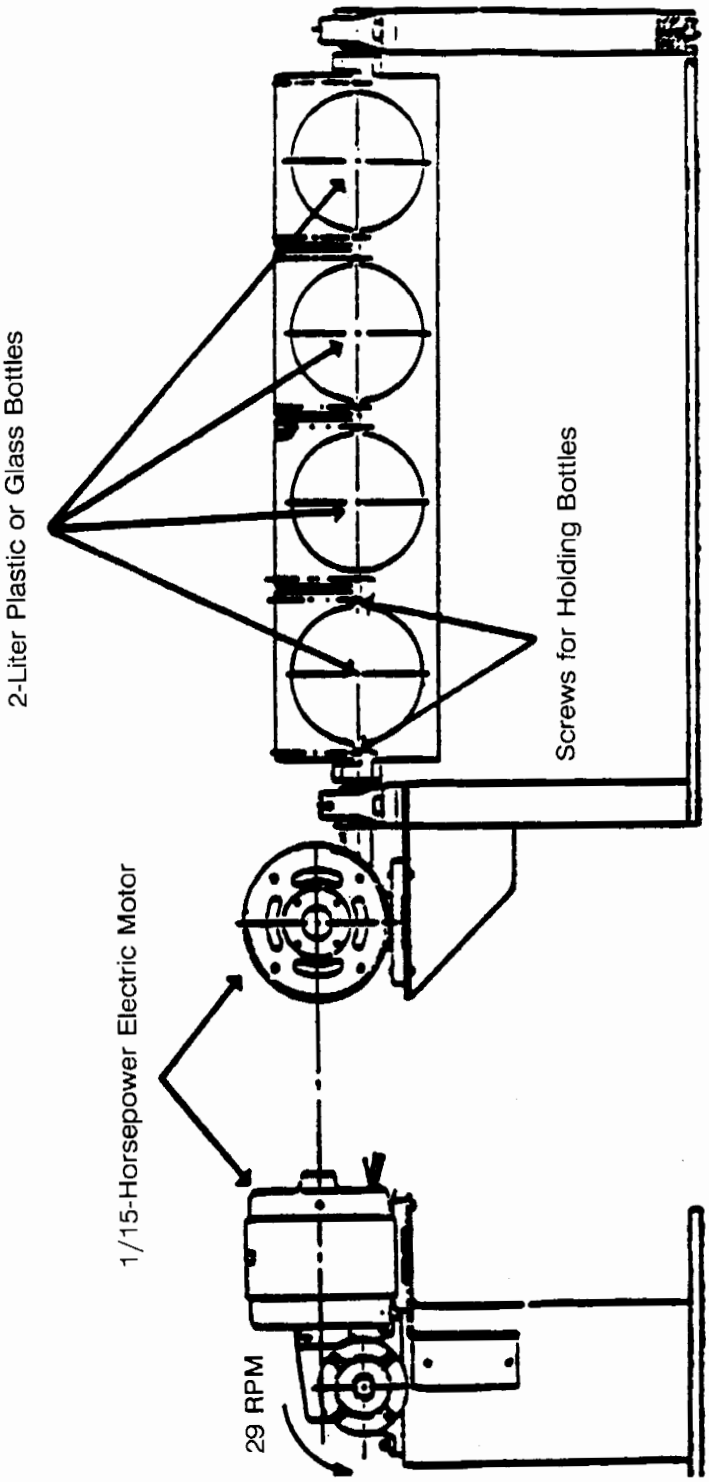


Figure 3. EPRI Extractor

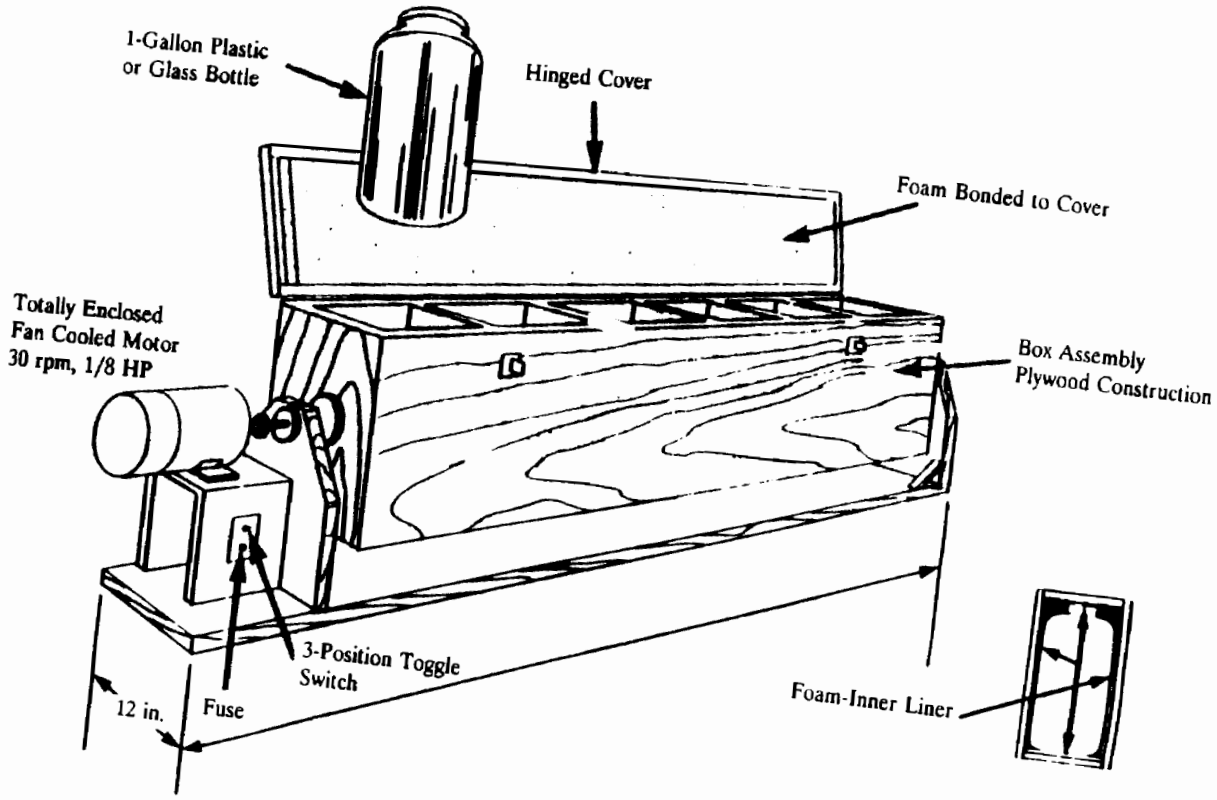
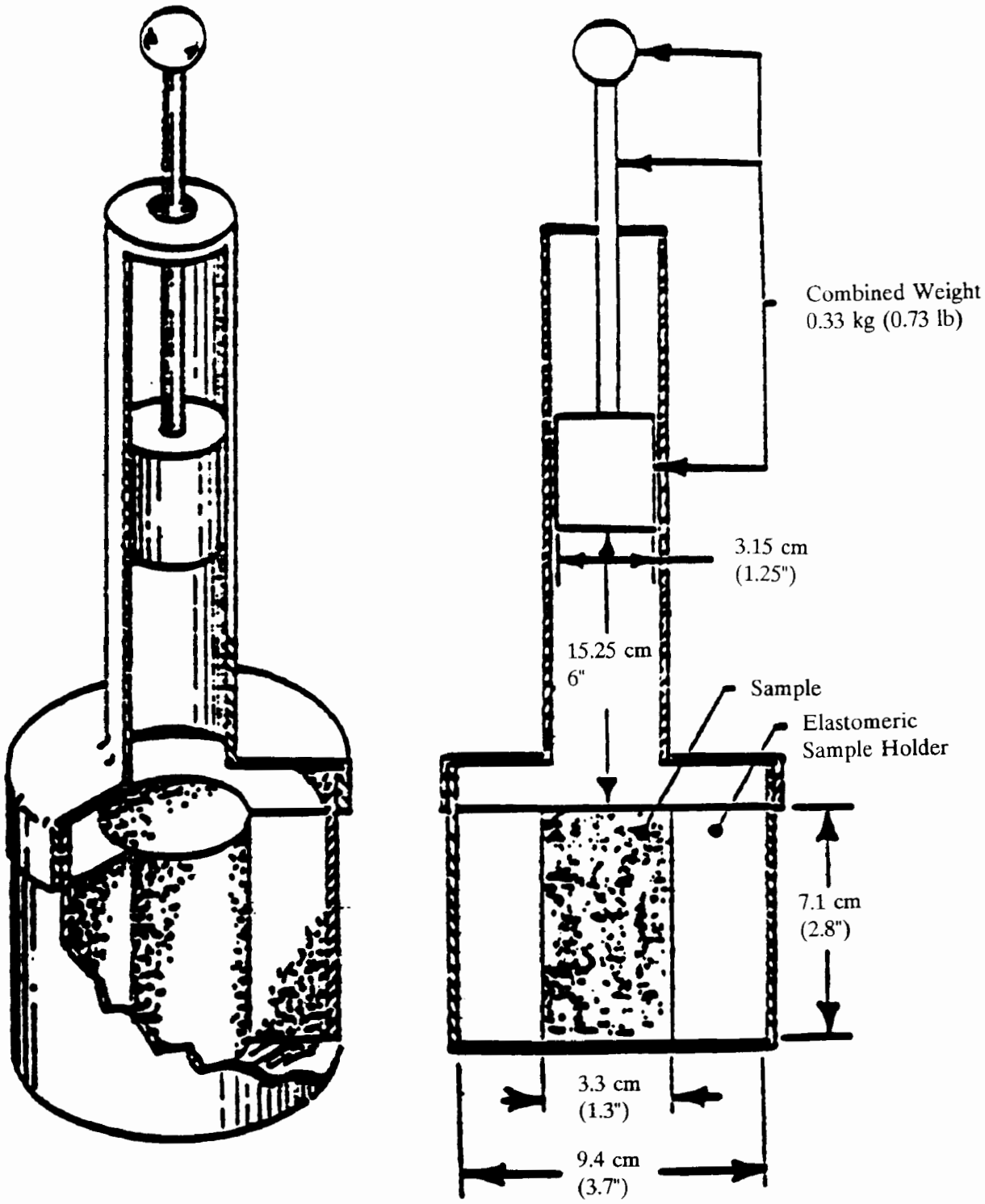
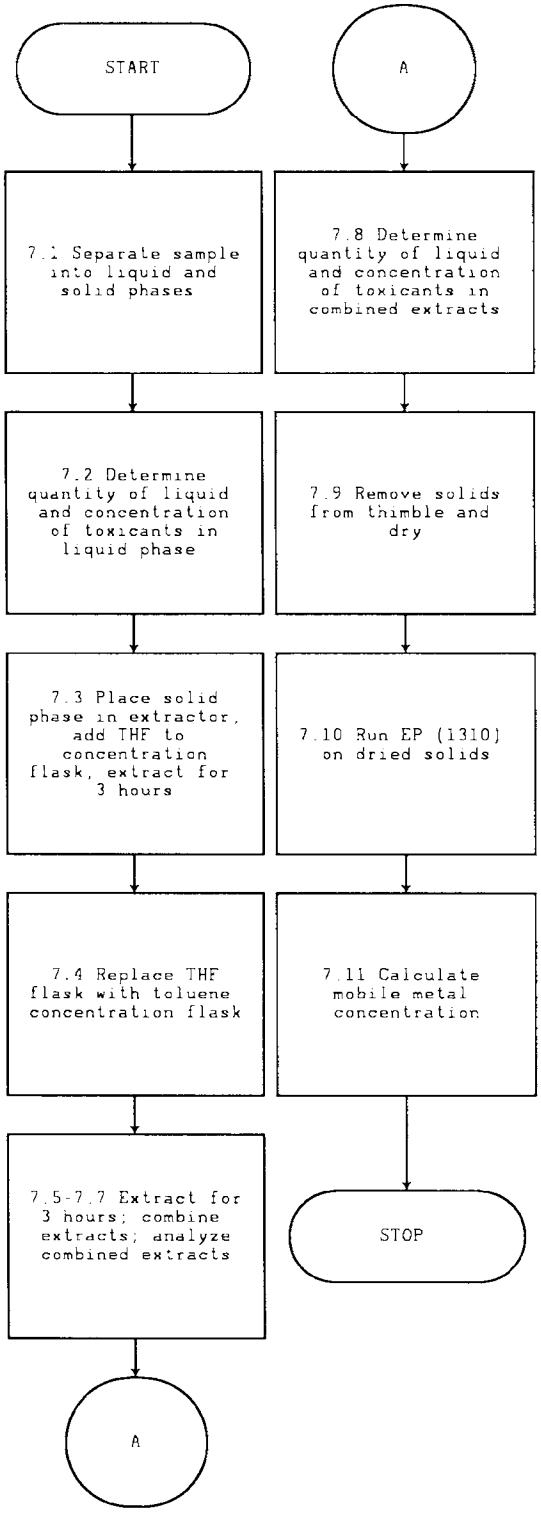


Figure 4. Compaction Tester




START
A
7.1 Separate sample into liquid and solid phases
7.8 Determine quantity of liquid and concentration of toxicants in combined extracts
7.2 Determine quantity of liquid and concentration of toxicants in liquid phase
7.9 Remove solids from thimble and dry
7.3 Place solid phase in extractor, add THF to concentration flask, extract for 3 hours
7.10 Run EP (1310) on dried solids
7.4 Replace THF flask with toluene concentration flask
7.11 Calculate mobile metal concentration
7.5-7.7 Extract for 3 hours; combine extracts; analyze combined extracts
STOP
A

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony**	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* ICP only
**May be analyzed by ICP, FLAA, or GFAA

1.2 When analyzing for total dissolved metals filter the sample, at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.45-µm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

Precipitation will cause a lowering of the silver concentration and therefore an inaccurate analysis.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes or equivalent.

4.2 Watch glasses or equivalent.

4.3 Qualitative filter paper and filter funnels.

4.4 Graduated cylinder or equivalent.

4.5 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Both plastic and glass containers are suitable.

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.45-µm filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with reagent water.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch. Refer to Chapter One for the proper protocol when analyzing spikes.

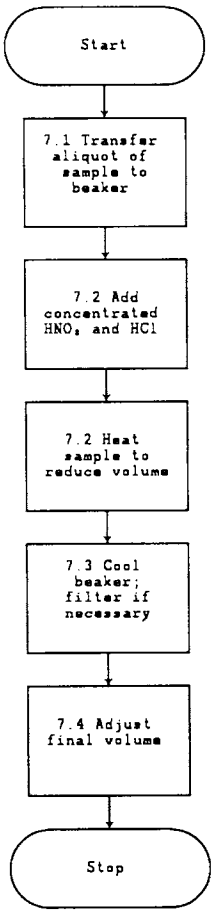
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer aliquot of sample to beaker
7.2 Add concentrated HNO_3 and HCl
7.2 Heat sample to reduce volume
7.3 Cool beaker; filter if necessary
7.4 Adjust final volume
Stop

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum	Magnesium
*Arsenic	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	*Selenium
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* Analysis by ICP

NOTE: See Method 7760 for the digestion and FLAA analysis of Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization. Consult Method 3020A for samples requiring graphite furnace analysis.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL or equivalent.

4.2 Watch glasses - Ribbed and plain or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Graduated cylinder or equivalent - 100mL.

4.5 Funnel or equivalent.

4.6 Hot plate or equivalent heating source - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (1:1), HCl. Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with

a ribbed watch glass or equivalent. Place the beaker on a hot plate or equivalent heating source and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is greater. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and delisting petitions (see Method 7000, Step 8.7). Although not

required, use of the method of standard addition is recommended for any sample that is suspected of having an interference.

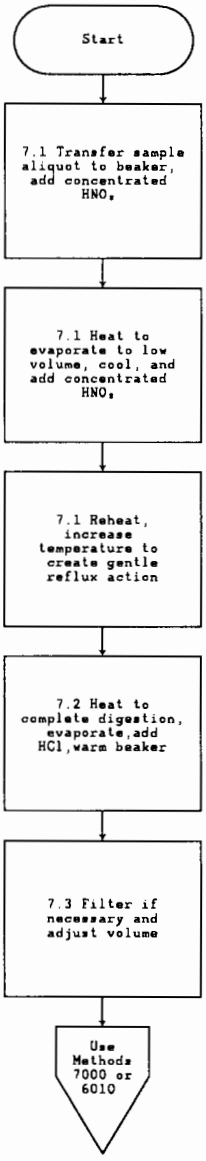
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer sample aliquot to beaker, add concentrated HNO3
7.1 Heat to evaporate to low volume, cool, and add concentrated HNO3
7.1 Reheat, increase temperature to create gentle reflux action
7.2 Heat to complete digestion, evaporate, add HCl, warm beaker
7.3 Filter if necessary and adjust volume
Use Methods 7000 or 6010

METHOD 3015

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA), graphite furnace absorption spectroscopy (GFAA), inductively coupled argon plasma spectroscopy (ICP), or inductively coupled argon plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3015.

1.2 Samples prepared by Method 3015 using nitric acid digestion may be analyzed by FLAA, GFAA, ICP-AES, or ICP-MS for the following:

Aluminum	Lead
Antimony	Magnesium
Arsenic*	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	Selenium*
Chromium	Silver
Cobalt	Sodium
Copper	Thallium
Iron	Vanadium
	Zinc

*Cannot be analyzed by FLAA

2.0 SUMMARY OF METHOD

2.1 A representative 45 mL aqueous sample is digested in 5 mL of concentrated nitric acid in a fluorocarbon (PFA or TFM) digestion vessel for 20 minutes using microwave heating. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle in a clean sample bottle prior to analysis.

3.0 INTERFERENCES

3.1 Many samples that contain organics, such as TCLP extracts, will result in higher vessel pressures which have the potential to cause venting of the vessels. Venting can result in either loss of analytes and/or sample, which

must be avoided. A smaller sample size can be used but the final water volume prior to nitric acid addition must remain at 45 mL. This is required to retain the heat characteristics of the calibration procedure. Limits of quantitation will change with sample quantity (dilution) as with instrumentation."

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Temperature monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psig) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psig).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several significant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vessels equipped with venting features, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.

CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the oven under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mechanisms or containers with fluorocarbon (PFA or TFM) liners and pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory grade microwave equipment is required to prevent safety hazards. For further information consult reference 1.

CAUTION: In addition, there are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Analytical balance, 300 g capacity, minimum accuracy ± 0.01 g.

4.5 Filter funnel, glass or disposable polypropylene.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 2).

5.3 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurities. If the method blank is less than the MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic containers are preferable. See Chapter Three, Step 3.1.3 of this manual, for further information.

6.3 Aqueous waste waters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100,99,98,97, 95,90,80,70,60,50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.1.4, and calculate the power setting corresponding to the required power in watts specified in the procedure from the (2-point) line. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2 °C). One kg of reagent water is weighed (1,000.0 g $\pm$ 0.1 g) into a fluorocarbon (PFA or TFM) beaker or a beaker made of some other

material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2 °C measured to ± 0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05 °C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2 °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship

$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t} \qquad \text{Eq. 1}$$

Where:

P = the apparent power absorbed by the sample in watts (W). ($W = joule \cdot sec^{-1}$)

K = the conversion factor for thermochemical calories·sec^{-1} to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat ($cal \cdot g^{-1} \cdot °C^{-1}$), of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 $cal \cdot g^{-1} \cdot °C^{-1}$) the calibration equation simplifies to:

$$P = (\Delta T)\ (34.86)$$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration power. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high solids (concentrated) samples and low solids (low concentration) samples all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours, rinsed with reagent water, and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. In addition, to avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and cap assembly to 0.01 g prior to use.

7.3.2 A 45 mL aliquot of a well shaken sample is measured in a graduated cylinder. This aliquot is poured into the digestion vessel with the number of the vessel recorded on the preparation sheet.

7.3.3 A blank sample of reagent water is treated in the same manner along with spikes and duplicates.

7.3.4 Add 5 mL of concentrated nitric acid to each vessel that will be used. Check to make sure the pressure relief disks are in the caps with the smooth side toward the sample and start the caps a few turns on the vessels. Finish tightening the caps in the capping station which will tighten them to a uniform torque pressure of 12 ft-lbs. (16 N-m) or to the manufacturers recommended specifications. Weigh each capped vessel to the nearest 0.01 g.

CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

7.3.5 Evenly distributed the vessels in the carousel according to the manufacturer's recommended specifications. Blanks are treated

as samples for the purpose of balancing the power input. When fewer than the recommended number of samples are digested, the remaining vessels should be filled with 45 mL of reagent water and 5 mL of nitric acid to achieve the full compliment of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 1).

7.3.6 Program the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. The chosen sequence will bring the samples to 160°C ± 4°C in 10 minutes and will permit a slow rise to 165-170 °C during the second 10 minutes (Ref. 3). Start the turntable motor and be sure the vent fan is running on high and the turntable is turning. Start the microwave generator.

7.3.6.1 Newer microwave units are capable of higher power that permit digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different power settings as long as they result in the same time and temperature conditions defined in 7.3.6. That is, any sequence of power that brings the samples to 160°C ± 4°C in 10 minutes and permits a slow rise to 165-170°C during the second 10 minutes (Ref. 2).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings are provided to reproduce the reaction conditions defined in 7.3.6, then these alternative vessels may be used (Ref. 1,3)

7.3.7 At the end of the microwave program, allow the vessels to cool for at least 5 minutes in the unit before removal to avoid possible injury if a vessel vents immediately after microwave heating. The samples may be cooled outside the unit by removing the carousel and allowing the samples to cool on the bench or in a water bath. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of the sample plus acid has decreased by more than 10% discard the sample.

7.3.8 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle or filtered.

7.3.8.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.8.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.8.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned cotainer.

7.3.9 The concentration values obtained from analysis must be corrected for the dilution factor from the acid addition. If the sample will be analyzed by ICP-MS additional dilution will generally be necessary. For example, the sample may be diluted by a factor of 20 with reagent water and the acid strength adjusted back to 10% prior to analysis. The dilutions used should be recorded and the measured concentrations adjusted accordingly (e.g., for a 45 mL sample and 5 mL of acid the correction factor is 1.11).

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One, of this Manual, should be followed.

8.2 For each analytical batch of samples processed, analytical reagent blanks (also field blanks if they were taken) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Duplicate samples should be processed on a routine basis. A duplicate sample is a real sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for a summary of performance data.

10.0 REFERENCES

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3. Kingston, H. M., Final Report EPA IAG #DWI3932541-01-I, September 30, 1988, Appendix A.

4. Shannon, M., Alternate Test Procedure Application, USEPA Region V, Central Regional Laboratory, 536 S. Clark Street, Chicago, IL 60606, 1989.

5. Kingston, H. M., Walter, P. J., "Comparison of Microwave Versus Conventional Dissolution for Environmental Applications", Spectroscopy, vol. 7 No. 9,20-27,1992.

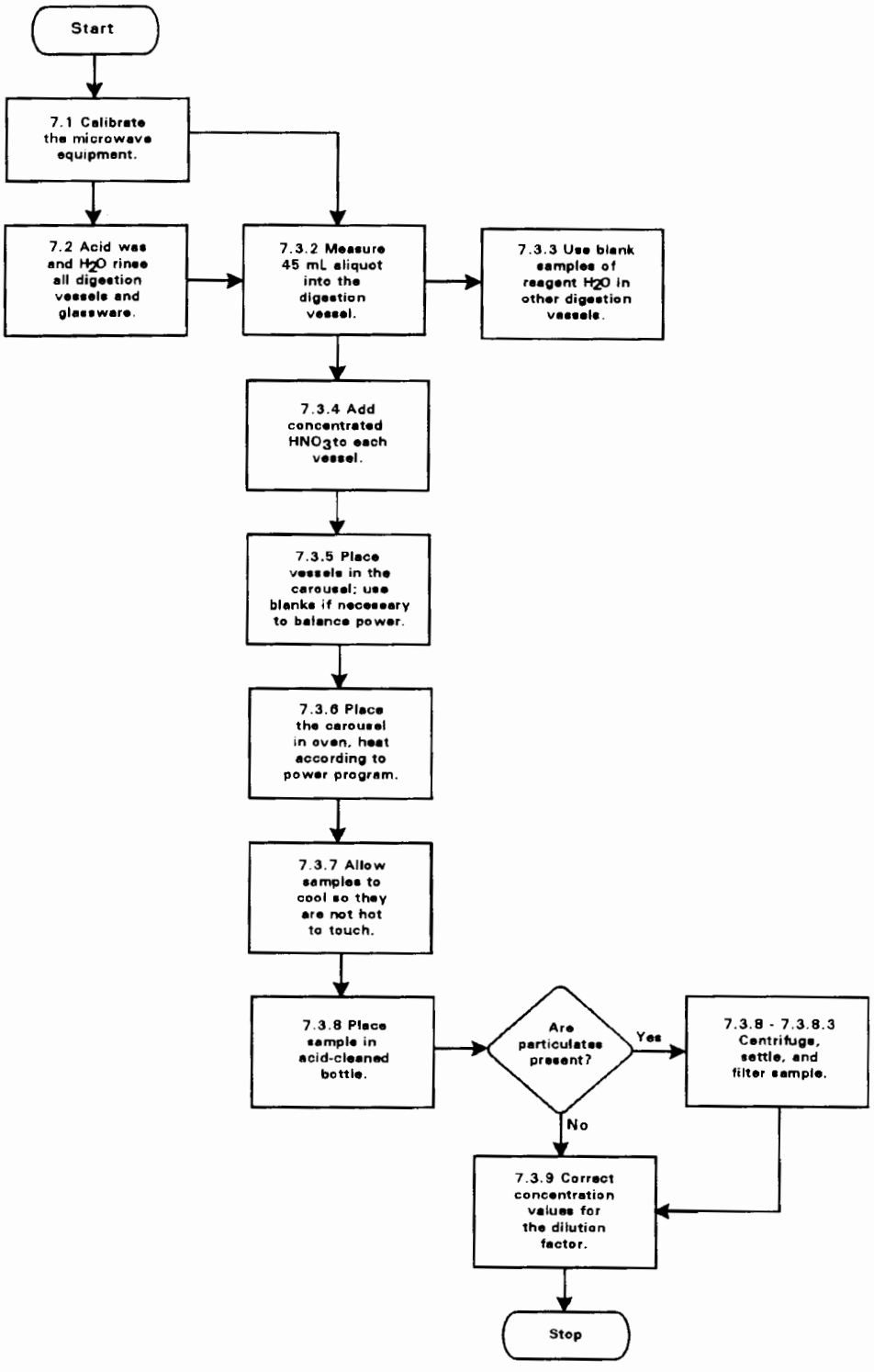
6. Sosinski, P., and Sze C., "Absolute Accuracy Study, Microwave Digestion Method 3015 (Nitric acid only)"; EPA Region III Central Regional Laboratory, 1991.

TABLE 1
MICROWAVE DIGESTION METHOD 3015 (Nitric Acid Only)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Al	Tm-11	510.0	485.5	26.3	5.4	-4.80%
Al	Tm-12	2687.0	2770.6	88.2	3.2	3.11%
Al	T-107	220.0	213.5	19.3	9.0	-2.95%
Al	T-109	113.0	117.7	30.6	2.6	4.16%
Ba	Tm-11	450.0	441.4	23.4	5.3	-1.90%
Ba	Tm-12	2529.0	2431.4	70.3	2.9	-3.86%
Ba	T-107	192.0	196.6	15.9	8.1	2.44%
Cd	Tm-11	40.8	44.6	2.1	4.7	9.46%
Cd	Tm-12	237.0	242.3	8	3.3	2.25%
Cd	T-107	14.3	12.4	0.9	7.2	-12.94%
Cd	T-109	12.1	10.3	1.7	16.5	-14.55%
Zn	Tm-11	55.4	55.9	2.6	4.6	1.06%
Zn	Tm-12	314.0	316.5	8.9	2.8	0.82%
Zn	T-107	75.8	81.6	3.3	4.0	7.68%
Zn	T-109	74.0	69.9	4.1	5.8	-5.46%
As	T-107	10.8	12.8	0.84	6.5	19.26%
As	T-109	8.15	90.6	11.0	12.2	11.26%
Co	Tm-11	227.0	242.6	14.1	5.8	6.90%
Co	Tm-12	1067.0	1153.3	35.9	3.1	8.09%
K	T-95	4700.0	5080.3	784	15.4	8.09%
K	T-109	2330.0	2601.5	383.4	14.7	11.65%
Ni	Tm-11	264.0	284.3	16.5	5.8	7.71%
Ni	Tm-12	1234.0	1293.0	39.4	3.0	4.79%
Ni	T-109	57.0	60.8	3.09	5.0	6.72%
Pb	Tm-11	275.0	275.9	32.2	11.7	0.36%
Pb	Tm-12	1326.0	1359.0	35.0	2.6	2.49%
Pb	T-107	26.0	30.0	0.2	0.66	15.65%
Pb	T-109	34.9	39.3	1.2	3.0	12.69%
Sb	WP980-1	16.9	18.3	0.47	2.6	8.27%
Sb	WP980-2	101.5	108.9	34.4	31.6	7.33%
Se	T-95	60.1	65.9	2.6	3.94	9.77%
Se	T-107	11.0	13.0	0.9	6.9	19.00%
Tl	WP980-1	50.0	55.1	2	3.6	10.26%
Tl	WP980-2	6.3	7.0	0.52	7.4	11.66%
V	Tm-11	491.0	532.6	26.1	4.9	8.48%
V	Tm-12	2319.0	2412.8	60.6	2.5	4.05%
Be	T-107	11.0	11.3	0.53	4.7	3.00%
Be	T-109	22.1	25.6	0.91	3.6	15.97%
Ca	T-107	11700.0	12364.0	783.6	6.3	5.68%
Ca	T-109	35400.0	38885.0	999	2.6	9.84%

TABLE 1 (continued)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Mg	T-95	32800.0	35002.0	1900	5.4	6.71%
Mg	T-107	2100.0	2246.7	110.5	4.9	6.99%
Mg	T-109	9310.0	10221.7	218.6	2.1	9.79%
Na	T-95	190000.0	218130.0	10700	4.9	14.81%
Na	T-107	20700.0	22528.0	1060	4.7	8.83%
Na	T-109	12000.0	13799.5	516.2	3.7	15.00%
Cr	Tm-11	52.1	64.3	4.1	6.4	23.51%
Cr	Tm-12	299.0	346.0	9.8	2.8	15.74%
Cr	T-107	13.0	22.3	1.5	6.7	71.77%
Cr	T-109	18.7	32.6	6.4	19.6	74.71%
Cu	Tm-11	46.3	76.5	4.4	5.7	65.36%
Cu	Tm-12	288.0	324.0	8.9	2.7	12.52%
Cu	T-107	30.0	42.3	4.0	9.4	41.17%
Cu	T-109	21.4	54.0	3.6	6.7	152.38%
Fe	Tm-11	249.0	289.3	16.4	5.7	16.18%
Fe	Tm-12	1089.0	1182.5	43.5	3.7	8.59%
Fe	T-107	52.0	63.8	8.7	13.6	22.69%
Fe	T-109	106.0	134.0	6.6	4.9	26.50%
Mn	Tm-11	46.0	60.9	3.2	5.2	32.48%
Mn	Tm-12	263.0	304.4	9.1	3.0	15.77%
Mn	T-107	45.0	52.6	3.1	5.9	17.09%
Mn	T-109	34.0	46.6	3.0	6.4	37.18%
Ag	WS378-1	46.0	19.4	5.6	2.9	-57.83%


Start
7.1 Calibrate the microwave equipment.
7.2 Acid was and H_2O rinse all digestion vessels and glassware.
7.3.2 Measure 45 mL aliquot into the digestion vessel.
7.3.3 Use blank samples of reagent H_2O in other digestion vessels.
7.3.4 Add concentrated HNO_3 to each vessel.
7.3.5 Place vessels in the carousel; use blanks if necessary to balance power.
7.3.6 Place the carousel in oven, heat according to power program.
7.3.7 Allow samples to cool so they are not hot to touch.
7.3.8 Place sample in acid-cleaned bottle.
Are particulates present?
Yes
7.3.8 - 7.3.8.3 Centrifuge, settle, and filter sample.
No
7.3.9 Correct concentration values for the dilution factor.
Stop

USEPA METHOD 3015A

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This microwave method is designed to perform extraction using microwave heating with nitric acid (HNO_3), or alternatively, nitric acid and hydrochloric acid (HCl). Since this method is not intended to accomplish total decomposition of the sample, the extracted analyte concentrations may not reflect the total content in the sample. This method is applicable to the microwave-assisted acid extraction/dissolution of available metals in aqueous samples, drinking water, mobility-procedure extracts, and wastes that contain suspended solids for the following elements:

Element		CASRN[a]
Aluminum	(Al)	7429-90-5*
Antimony	(Sb)	7440-36-0*
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3*
Beryllium	(Be)	7440-41-7*
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3*
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6*
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4*
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4*
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2*
Zinc	(Zn)	7440-66-6

[a]Chemical Abstract Service Registry Number

*Elements which typically require the addition of HCl for optimum recoveries. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec. 9.0).

1.2 This method provides options for improving the performance for certain analytes, such as antimony, iron, aluminum, and silver by the addition of hydrochloric acid, when necessary. It is intended to provide a rapid multi-element acid extraction prior to analysis so that decisions can be made about materials and site clean-up levels, and as an estimate of metal toxicity. Digests produced by the method are suitable for analysis by inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), flame atomic absorption spectrophotometry (FLAA), and graphite furnace atomic absorption spectrophotometry (GFAA). However, the addition of HCl may limit the methods of detection, or increase the difficulties of detection with some techniques.

Due to the rapid advances in microwave technology, consult the manufacturer's recommended instructions for guidance on their microwave digestion system. This method is generic and may be implemented using a wide variety of laboratory microwave equipment.

2.0 SUMMARY OF METHOD

2.1 A representative 45 mL aqueous sample is extracted in 5 mL concentrated nitric acid or, optionally, 4 mL concentrated nitric acid and 1 mL concentrated hydrochloric acid, for 20 minutes using microwave heating with a suitable laboratory microwave unit. The temperature of the acid-sample mixture is brought to 170 ± 5 °C in 10 minutes, and maintained at 170 ± 5 °C for 10 minutes to accelerate the leaching process. The sample and acid(s) are placed in a fluorocarbon polymer (such as PFA or TFM) or quartz microwave vessel or vessel liner. The vessel is sealed and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate determinative method.

3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for a listing of applicable definitions.

4.0 INTERFERENCES

4.1 Digestion of samples which contain organics will create high pressures due to the evolution of gaseous digestion products. This may cause venting of the vessels with potential loss of sample components and/or analytes. When warranted by the potential reactivity of the sample, a smaller sample size may be used, and the concentration for final calculations adjusted, but the final water volume prior to addition of acid(s) is recommended to be 45 mL. This is recommended in order to retain the heat characteristics of the calibration procedure if used. Variations of the method, due to very reactive materials, are specifically addressed in Section 11.3.3. Limits of quantitation will change with sample quantity (dilution) and with instrumentation.

4.2 Many samples can be dissolved by this method. However, when the sample contains suspended solids which are made up of refractory compounds, such as silicon dioxide, titanium dioxide, alumina, and other oxides, they will not be dissolved and in some cases may sequester target analyte elements. These bound elements are considered nonmobile in the environment and are excluded from most aqueous pollutant transport mechanisms.

5.0 SAFETY

5.1 The microwave unit cavity must be corrosion resistant and well ventilated. All electronics must be well protected against corrosion for safe operation.

CAUTION: *There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. A listing of these specific suggestions is beyond the scope of this method. The analyst is advised to consult the*

equipment manual, the equipment manufacturer, and other appropriate literature for proper and safe operation of the microwave equipment and vessels. For further details and safety literature, references 1, 7 and 8 review methods and safety in microwave sample preparation.

5.2 The method requires microwave transparent and reagent resistant materials such as fluorocarbon polymers (examples are PFA and TFM) or quartz to contain acids and samples. For higher pressure capabilities, the vessel may be contained within layers of different microwave transparent materials for strength, durability, and safety. The internal volume of the vessel should be at least 100 mL, and the vessel must be capable of withstanding pressures of at least 30 atm (435 psi), and capable of controlled pressure relief. These specifications are to provide an appropriate, safe, and durable reaction vessel of which there are many adequate designs by many suppliers.

CAUTION: *The outer layers of vessels are frequently not as acid or reagent resistant as the liner material. In order to retain the specified performance and safety requirements, these outer layers must not be chemically degraded or physically damaged. Routine examination of the vessel materials is necessary to ensure their safe use.*

CAUTION: *Another safety concern relates to the use of sealed containers without pressure relief devices. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures, but must be safely contained. Some digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures. Only fluorocarbon (such as PFA, TFM, and others) or quartz containers with pressure relief mechanisms or containers with fluorocarbon or quartz liners and pressure relief mechanisms are considered acceptable.*

CAUTION: *An aqueous sample must contain no more than 1% (V/V or g/V) oxidizable organic material. Upon oxidation, organic material, whether liquid or solid, contributes to gaseous digestion products. Pressure build-up above the pressure limit will result in venting of the closed digestion vessel.*

CAUTION: *Laboratories should not use domestic (kitchen) type microwave ovens for this method because of significant safety issues. When acids such as nitric and hydrochloric are used to effect sample digestion in microwave units in open or sealed vessel(s), there is the potential for acid vapors released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a system with isolated and corrosion resistant instrument components and safety devices prevents this from occurring.*

Users are advised not to use domestic (kitchen) type microwave ovens or sealed containers which are not equipped with controlled pressure relief mechanisms for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details, consult references 1, 7, and 8.

6.0 EQUIPMENT AND SUPPLIES

6.1 Microwave apparatus requirements

6.1.1 The temperature performance requirements necessitate the microwave decomposition system to sense the temperature to within ± 2.5 °C and automatically adjust the microwave field output power within 2 seconds of sensing. Temperature sensors should be accurate to ± 2 °C (including the final reaction temperature of 170 ± 5 °C). Temperature feedback control provides the primary performance mechanism for the method. Due to the variability in sample matrix types and microwave digestion equipment (i.e., different vessel types and microwave oven designs), temperature feedback control is preferred for reproducible microwave heating. For further details, consult reference 7.

Alternatively, for a specific vessel type, specific set of reagent(s), and sample type, a calibration control mechanism can be developed similar to those described in previous microwave methods (See EPA Method 3051). Through calibration of the microwave power for a specific number and type of vessel, vessel load, and heat loss characteristics of a specific vessel series, the reaction temperature profile described in Section 11.3.5 can be reproduced (Reference 7). The calibration settings are specific for the number and type of vessel and microwave system being used, in addition to the specific reagent combination being used. Therefore, no specific calibration settings are provided in this method. These settings may be developed by using temperature monitoring equipment for each specific set of microwave equipment and vessel type. They may be used as previously described in EPA Methods 3052 and 3051. In this circumstance, the microwave system provides programmable power, which can be programmed to within ±12 W of the required power. Typical systems provide 600 W - 1200 W of power. Calibration control provides backward compatibility with older laboratory microwave systems which may not be equipped for temperature monitoring or feedback control and with lower cost microwave systems for some repetitive analyses. Older vessels with lower pressure capabilities may not be compatible (References 4 - 8).

6.1.2 The accuracy of the temperature measurement system should be periodically validated at an elevated temperature. This can be done using a container of silicon oil (a high temperature oil) and an external, calibrated temperature measurement system. The oil should be adequately stirred to ensure a homogeneous temperature, and both the microwave temperature sensor and the external temperature sensor placed into the oil. After heating the oil to a constant temperature of 170 ± 5°C, the temperature should be measured using both sensors. If the measured temperatures vary by more than 1 to 2°C, the microwave temperature measurement system should be calibrated. Consult the microwave manufacturer's instructions about the specific temperature sensor calibration procedure (see EPA Method 3052).

6.1.3 A rotating turntable is employed to ensure the homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm. Other types of equipment that are used to assist in achieving uniformity of the microwave field may also be appropriate.

6.2 Class A or appropriate mechanical pipette, volumetric flask, or graduated cylinder, 50 or 100 mL capacity or equivalent.

6.3 Filter paper, qualitative or equivalent.

6.4 Filter funnel, glass, polypropylene, or other appropriate material.

6.5 Analytical balance, of appropriate capacity and resolution, meeting data quality objectives.

7.0 REAGENTS

7.1 All acids should be sub-boiling distilled and/or high purity where possible to minimize blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without decreasing the accuracy of the determination. If the purity of a reagent is questionable, the reagent should be analyzed to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

7.1.1 Concentrated nitric acid (HNO_3). The acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

7.1.2 Concentrated hydrochloric acid (HCl). The acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

7.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. For further details, consult Reference 2.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of SW-846. Refer to that chapter, as updated, for guidance.

8.2 All sample containers must be prewashed with acids, water, and metal-free detergents, if necessary, depending on the use history of the container (Reference 7). Plastic and glass containers are both suitable. For further information, see Chapter Three.

8.3 Aqueous wastewaters must be acidified to a pH < 2 with HNO_3.

9.0 QUALITY CONTROL

9.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts.

9.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analysis process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., wastewaters, extracts, etc.).

9.3 Spiked samples or standard reference materials should be included with each group of samples processed, or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

9.4 Periodically, the accuracy of the temperature measurement system used to control the microwave equipment should be validated per Section 6.1.2.

9.5 (Not necessary if using temperature feedback control.) Each day that samples are extracted, the microwave-power calibration should be verified by heating 1 kg of ASTM Type II water (at 22 ± 3 °C) in a covered, microwave-transparent vessel for 2 min at the setting for 490 W and measuring the water temperature after heating per Section 10.1.5. If the power calculated (per Section 12) differs from 490 W by more than ± 10 W, the microwave settings should be recalibrated per Section 10.0.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration of Microwave Equipment

NOTE: *If the microwave unit uses temperature feedback control to control the performance specifications of the method, then performing the calibration procedure is not necessary.*

10.1.1 Calibration is the normalization and reproduction of a microwave field strength to permit reagent and energy coupling in a predictable and reproducible manner. It balances reagent heating and heat loss from the vessels and is equipment dependent due to the heat retention and loss characteristics of the specific vessel. Available power is

evaluated to permit the microwave field output in watts to be transferred from one microwave system to another.

Use of calibration to control this reaction requires balancing output power, coupled energy, and heat loss to reproduce the temperature heating profile given in section 11.3.5. The conditions for each acid mixture and each batch containing the same specified number of vessels must be determined individually. Only identical acid mixtures and vessel models and specified numbers of vessels may be used in a given batch.

10.1.2 For cavity type microwave equipment, calibration is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the system. The calibration format required for laboratory microwave systems depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few systems have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (see Section 10.1.4). Otherwise, the analyst must use the multiple point calibration method (see Section 10.1.3). Assistance in calibration and software guidance of calibration are available in References 7 and 8.

10.1.3 Multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured: 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in Section 10.1.5. This data is clustered about the customary working power ranges. Nonlinearity has been encountered at the upper end of the calibration. If the system's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (± 10 W), then the entire calibration should be re-evaluated.

10.1.4 The three-point calibration involves the measurement of absorbed power at three different power settings. Power is measured at 100% and 50% using the procedure described in Section 10.1.5. From this 2-point line, determine the partial power setting that corresponds to the power, in watts, specified in the procedure to reproduce the heating profile specified in Section 11.3.6. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ± 10 W, use the multiple point calibration in Section 10.1.3. This point should also be used to periodically verify the integrity of the calibration.

10.1.5 Equilibrate a large volume of water to room temperature (22 ± 3 °C). One kg of reagent water is weighed (1,000.0 ± 0.1 g) into a fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 22 ± 3 °C measured to ± 0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the system's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water is vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation (irradiating with the stir bar in the vessel could cause electrical arcing) and record the maximum temperature within the first 30 seconds to ± 0.05 °C. Use a new sample for each additional measurement. If the water is reused (after making adjustments for any loss of weight due to heating), both the water and the beaker must have returned to 22 ± 3 °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Eq. 1

Where:

P = the apparent power absorbed by the sample in watts (W) (joule sec^{-1})

K = the conversion factor for thermochemical calories sec^{-1} to watts (K= 4.184)

C_p = the heat capacity, thermal capacity, or specific heat (cal g^{-1} °C^{-1}) of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes (120 sec) and 1 kg (1000 g) of distilled water (heat capacity at 25 °C is 0.9997 cal g^{-1} °C^{-1}), the calibration equation simplifies to:

Eq. 2

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification. During measurement and operation the line voltage should not vary by more than ± 2 V (Reference 7). Electronic components in most microwave units are matched to the system's function and output. When any part of the high voltage circuit, power source, or control components in the system have been serviced or replaced, it will be necessary to recheck the system's calibration. If the power output has changed significantly (± 10 W), then the entire calibration should be re-evaluated.

11.0 SAMPLE PROCEDURE

11.1 Temperature control of closed vessel microwave instruments provides the main feedback control performance mechanism for the method. Method control requires a temperature sensor in one or more vessels during the entire digestion. The microwave decomposition system should sense the temperature to within ± 2.5 °C and permit adjustment of the microwave output power within 2 seconds.

11.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between highly concentrated samples and low concentrated samples, all digestion vessels (fluoropolymer or quartz liners) should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80 °C, but less than boiling) for a minimum of two hours followed by hot (1:1) nitric acid (greater than 80 °C, but less than boiling) for a minimum of two hours. The vessels should then be rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of

the digestion vessels is unknown or cross contamination from prior sample digestions in vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific material used and then rinsed with reagent water and dried in a clean environment.

11.3 Sample Digestion

11.3.1 Measure a 45 mL aliquot of a well-shaken, homogenized sample using an appropriate volumetric measurement and delivery device, and quantitatively transfer the aliquot to an appropriate vessel equipped with a controlled pressure relief mechanism.

11.3.2 Add 5 ± 0.1 mL concentrated nitric acid or, alternatively, 4 ± 0.1 mL concentrated nitric acid and 1 ± 0.1 mL concentrated hydrochloric acid to the vessel in a fume hood (or fume exhausted enclosure). The addition of concentrated hydrochloric acid to the nitric acid is appropriate for the stabilization of certain analytes, such as Ag, Ba, and Sb and high concentrations of Fe and Al in solution. Improvements and optimal recoveries of antimony and silver upon addition of HCl have been described in the literature (Reference 7). The addition of hydrochloric acid may, however, limit the detection techniques or increase the difficulties of analysis for some detection systems.

CAUTION: *The addition of hydrochloric acid must be in the form of concentrated hydrochloric acid and not from a premixed combination of acids. A build-up of chlorine gas, as well as other gases, will result from a premixed acid solution. These gases may be violently released upon heating. This is avoided by adding the acid in the described manner.*

CAUTION: *Toxic nitrogen oxide(s) and chlorine fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a properly operating fume ventilation system.*

CAUTION: *The analyst should wear protective gloves and face protection.*

CAUTION: *The use of microwave equipment with temperature feedback control is required to control any unfamiliar reactions that may occur during the leaching of samples of unknown composition. The leaching of these samples may require additional vessel requirements such as increased pressure capabilities.*

11.3.3 The analyst should be aware of the potential for a vigorous reaction, especially with samples containing suspended solids composed of volatile or easily oxidized organic species. When digesting a matrix of this type, if a vigorous reaction occurs upon the addition of reagent(s), this sample represents a safety hazard. Do not leach the sample as described in this method due to the high potential for unsafe and uncontrollable reactions.

11.3.4 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and, when applicable, connect appropriate temperature and pressure monitoring equipment to vessels according to manufacturer’s specifications.

11.3.5 This method is a performance based method, designed to achieve or approach consistent leaching of the sample through achieving specific reaction conditions. The temperature of each sample should rise to 170 ± 5 °C in approximately 10 minutes and remain at 170 ± 5 °C for 10 minutes, or for the remainder of the twenty-minute digestion period (References 3, 4, 6, and 7). The time vs. temperature and pressure profiles for the leaching of three simulated wastewater samples using Method 3015 are shown in Figure 1. The samples are composed of approximately 0.35 g SRM 2704 (Buffalo River Sediment) mixed in 45 mL double-deionized water. The figure demonstrates the temperature and pressure profiles for both the all-nitric digest (5 mL

concentrated nitric acid), and the nitric and hydrochloric mixed-acid digest (4 mL concentrated nitric acid and 1 mL concentrated hydrochloric acid). Also shown is the profile for the heating of the wastewater sample without addition of acids. When using temperature feedback control, the number of samples that may be simultaneously digested may vary, from one sample up to the maximum number of vessels that can be heated by the magnetron of the microwave unit according to the heating profile specified in this section. (The number will depend on the power of the unit, the number of vessels, and the heat loss characteristics of the vessels (Reference 7)).

11.3.5.1 Calibration control is applicable in reproducing this method provided the power in watts versus time parameters are determined to reproduce the specifications listed in Section 11.3.5. The calibration settings will be specific to the quantity of reagents, the number of vessels, and the heat loss characteristics of the vessels (Reference 7). If calibration control is being used, any vessels containing acids for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with 45 mL water, and the acid mixture added, so that the full complement of vessels is achieved. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbing mass in the cavity (Reference 7). Irradiate each group of vessels using the predetermined calibration settings. (Different vessel types should not be mixed.)

11.3.6 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave system. Cooling of the vessels may be accelerated by internal or external cooling devices. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained their seal throughout the digestion. Due to the wide variability of vessel designs, a single procedure is not appropriate. For vessels that are sealed as discrete separate entities, the vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of the sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised. For vessels with burst disks, a careful visual inspection of the disk, in addition to weighing, may identify compromised vessels. For vessels with resealing pressure relief mechanisms, an auditory or a physical sign that can indicate whether a vessel has vented is appropriate.

11.3.7 Complete the preparation of the sample by carefully uncapping and venting each vessel in a chemical fume hood (or fume exhausted enclosure). Vent the vessels using the procedure recommended by the vessel manufacturer. Quantitatively transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged (Section 11.3.7.1), allowed to settle (Section 11.3.7.2), or filtered (Section 11.3.7.3).

11.3.7.1 Centrifugation: Centrifugation at 2,000 - 3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

11.3.7.2 Settling: If undissolved material, such as SiO_2, TiO_2, or other refractory oxides, remains, allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

11.3.7.3 Filtering: If necessary, the filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

11.3.8 The removal or reduction of the quantity of sample may be desirable for concentration of analytes prior to analysis. The chemistry and volatility of the analytes of interest should be considered and evaluated when using this alternative (Reference 7, 8). Sample evaporation in a controlled environment with controlled purge gas and neutralizing and collection of exhaust interactions is an alternative where appropriate. This manipulation may be performed in the microwave system, if the system is capable of this function, or external to the microwave system in more common apparatus(s). This option must be tested and validated to determine analyte retention and loss and should be accompanied by equipment validation possibly using the standard addition method and standard reference materials. For further information, see References 7 and 8 and Method 3052.

NOTE: *The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable. Waste minimization techniques should be used to capture reagent fumes. This procedure should be tested and validated in the apparatus and on standards before using on unknown samples.*

11.3.9 Transfer or decant the sample into volumetric ware and dilute the digest to a known volume. The digest is now ready for analysis for elements of interest using appropriate elemental analysis techniques and/or SW-846 methods.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculations: The concentrations determined are to be reported on the basis of the actual volume of the original sample.

12.2 Prior to use of the method, verify that the temperature sensing equipment is properly reading temperature. A procedure for verification is given in Section 6.1.2. This will establish the accuracy and precision of the temperature sensing equipment, which should be carried throughout the statistical treatment of the quality assurance data.

12.3 In calibrating the microwave unit (Section 10.0), the power absorbed (for each power setting) by 1 kg of reagent water exposed to 120 seconds of microwave energy is determined by the expression:

$$\text{Power (in watts)} = (T_1 - T_2)\ (34.86)$$

where: T_1 = Initial temperature of water (between 21 and 25 °C to nearest 0.1 °C)

T_2 = Final temperature of water (to nearest 0.1 °C)

12.4 Plot the power settings against the absorbed power (calculated in Section 12.3) to obtain a calibration relationship. Alternatively, use a microwave calibration program to analyze the calibration data (References 7 and 8). Interpolate the data to obtain the instrument settings needed to provide the wattage levels specified in Section 12.3.

13.0 METHOD PERFORMANCE

13.1 The fundamental analytical validation of Method 3015 with nitric acid has been performed (Reference 6). The results are shown in Table 1. Variations of 3015 including nitric acid and hydrochloric acid have also been published in the literature (References 5, 7, 9). The method has also been tested on a variety of matrices, including two simulated wastewater

matrices, one consisting of ~ 0.35 g sediment (SRM 2704) mixed with 45 mL double-deionized water, and the other consisting of ~ 0.35 g soil (SRM 4355) mixed with 45 mL double-deionized water. The results are shown in Tables 2 and 3, and are published in the literature (Reference 9).

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036, (202) 872-4477.

16.0 REFERENCES

1. Kingston, H.M.; Jassie, L.B. In Introduction to Microwave Sample Preparation: Theory and Practice; Kingston, H. M. and Jassie, L. B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988; Chapters 6 and 11.

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3. Kingston, H. M., Final Report EPA IAG #DWI3932541-01-I, September 30, 1988, Appendix A.

4. Shannon, M., Alternate Test Procedure Application, USEPA Region V, Central Regional Laboratory, 536 S. Clark Street, Chicago, IL 60606, 1989.

5. Kingston, H. M., Walter, P. J., "Comparison of Microwave Versus Conventional Dissolution for Environmental Applications", Spectroscopy, Vol. 7 No. 9, 20-27, 1992.

6. Sosinski, P., and Sze, C., "Absolute Accuracy Study, Microwave Digestion Method 3015 (nitric acid only)"; EPA Region III Central Regional Laboratory, 1991.

7. Kingston, H. M., Haswell, S. J., Eds. Microwave Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications; ACS Professional Reference Book Series; American Chemical Society: Washington, DC 1997.

8. Duquesne University. Analytical Sample Preparation and Microwave Chemistry Center. *SamplePrep Web*. Access http://www.sampleprep.duq.edu/

9. Link, D.D., Kingston, H.M., Walter, P.J., “Development and Validation of the New EPA Microwave-Assisted Leach Methods 3051A and 3015A.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 3, Figure 1, and a flow diagram of method procedure.

TABLE 1

RESULTS OF VALIDATION STUDY FOR METHOD 3015 (NITRIC ONLY)

(REFERENCE 6)

	TM-11		TM-12		T-95		T-107		T-109	
Element	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**
Al	480	26	2800	88.			210	19	120	31
As							13	1	90	11
Ba	140	23	2400	70			200	16		
Be							11.3	0.5	26	1
Ca							12000	783	59000	999
Cd	45	2	240	8			12	1	10	2
Co	240	14	1150	36						
Cr	64	4	350	10			23	1	30	6
Cu	78	4	320	9			42	4	34	4
Fe	290	16	1180	43			60	9	130	7
K					5000	784			2600	383
Mg					35000	1922	2200	110	10200	218
Mn	61	3	300	9			53	3	47	3
Na					20000	10690	2300	1056	13800	516
Ni	280	16	1290	39					61	2
Pb	280	32	1360	35			30.1	0.2	39	1
Se					65.97	2.65	13	1		
V	530	26	2400	61						
Zn	56	3	520	9			31	3	70	4

	WP980 #1		WP980 #2		WS378 #4		WS378 #12	
Element	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**	**Mean**	**Std Dev**
Sb	18.0	0.5	110	34				
Tl	55	2	7.0	0.5				
Ag					ND		19	5

TABLE 2

COMPARISON OF ANALYTE RECOVERIES FROM “SIMULATED WASTEWATER” MIXTURE OF ~ 0.35 G SRM 2704 (BUFFALO RIVER SEDIMENT) AND 45 ML DOUBLE-DEIONIZED WATER USING BOTH DIGEST OPTIONS OF METHOD 3015

(REFERENCE 9)

Element	5 mL HNO_3	4 mL HNO_3 +	Total Analyte

Results reported in μg/g analyte (mean ± 95% confidence limit).

Total concentrations are taken from NIST SRM Certificate of Analysis.

Values in parenthesis are reference concentrations.

* The total concentration of this analyte in SRM 2704 is not certified.

TABLE 3

COMPARISON OF ANALYTE RECOVERIES FROM “SIMULATED WASTEWATER” MIXTURE OF ~0.35 G SRM 4355 (PERUVIAN SOIL) AND 45 ML DOUBLE-DEIONIZED WATER USING BOTH DIGEST OPTIONS OF METHOD 3015

(REFERENCE 9)

Element	5 mL HNO_3	4 mL HNO_3 +	Total Analyte

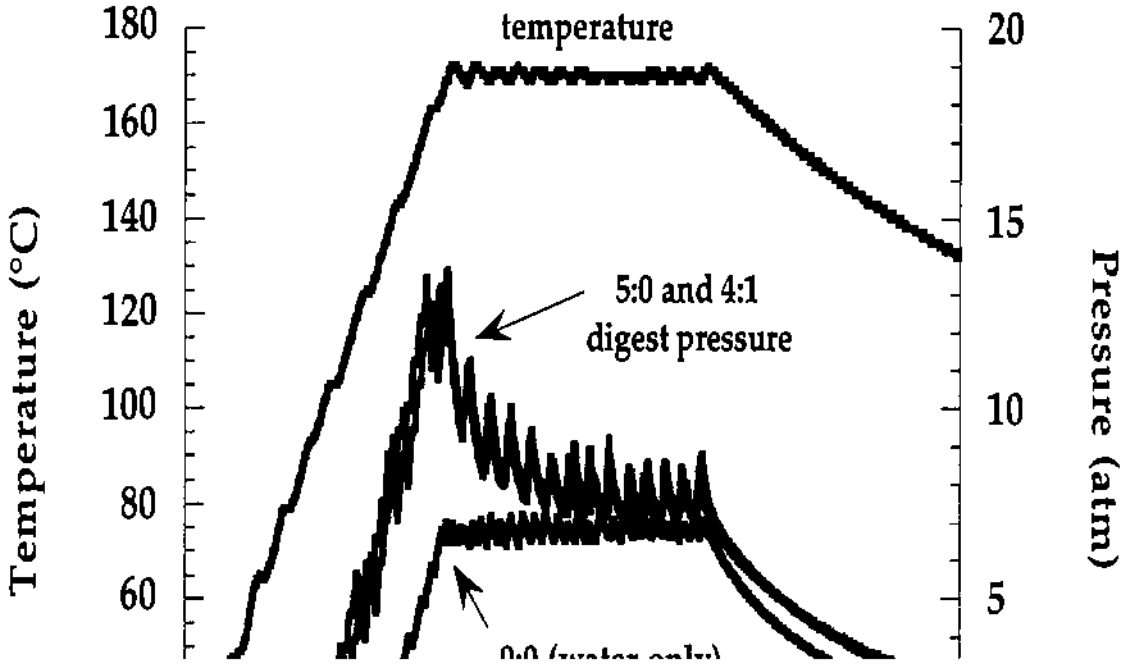
Results reported in μg/g analyte (mean ± 95% confidence limit).

Total concentrations are taken from NIST SRM Certificate of Analysis.

* Values in parenthesis are reference concentrations

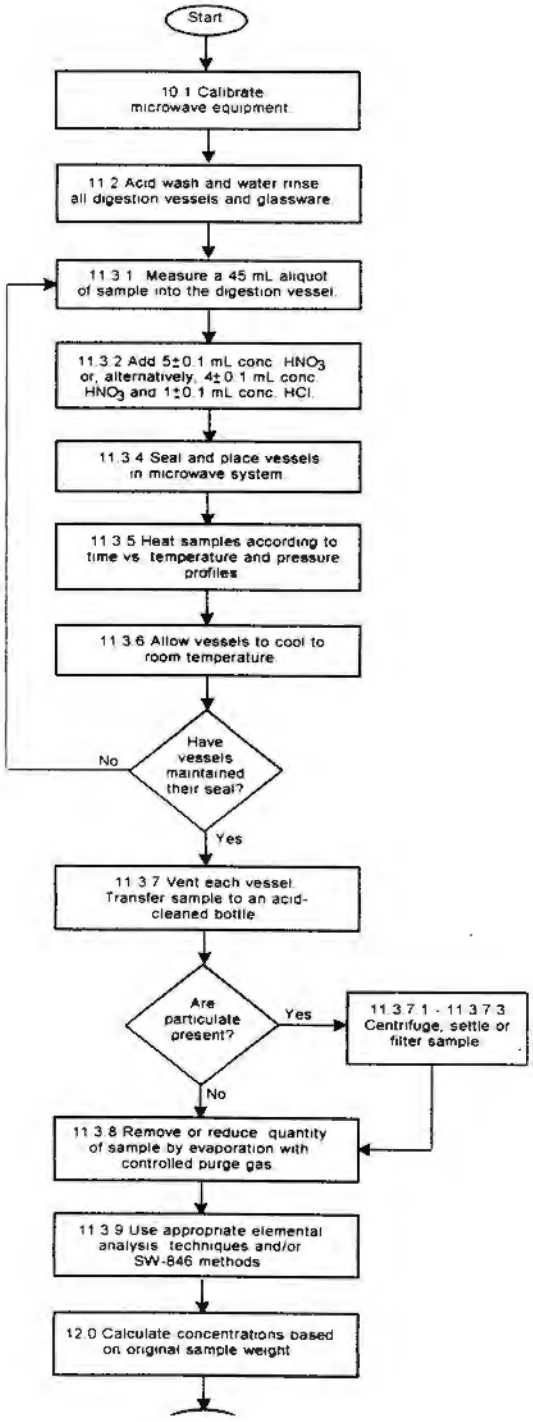
.FIGURE 1

THE TYPICAL TEMPERATURE AND PRESSURE PROFILE FOR THE HEATING OF A SIMULATED WASTEWATER SAMPLE (~ 0.35 G SRM 2704 + 45 ML DOUBLE-DEIONIZED WATER) USING BOTH DIGEST OPTIONS (5 ML HNO_3 AND 4 ML HNO_3 + 1 ML HCL) OF METHOD 3015.



METHOD 3015A

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS



METHOD 3020A

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS
FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis by furnace atomic absorption spectroscopy (GFAA) for the metals listed below. The procedure is used to determine the total amount of the metal in the sample.

1.2 Samples prepared by Method 3020 may be analyzed by GFAA for the following metals:

Beryllium	Lead
Cadmium	Molybdenum
Chromium	Thallium
Cobalt	Vanadium

NOTE: For the digestion and GFAA analysis of arsenic and selenium, see Methods 7060 and 7740. For the digestion and GFAA analysis of silver, see Method 7761.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) nitric acid. This percentage will vary depending on the amount of acid used to complete the digestion. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL, or equivalent.

4.2 Watch glasses - ribbed or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Funnel or equivalent.

4.5 Graduated Cylinder - 100mL.

4.6 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a non-ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL); use a ribbed watch glass, not allowing any portion of the bottom of the beaker to go dry. Remove the beaker and add approximately 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

7.3 Remove the beaker from the hot plate and wash down the beaker walls and watch glass with water. When necessary, filter or centrifuge the sample to remove silicates and other insoluble material that may interfere with injecting the sample into the graphite atomizer. (This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.) Adjust to the final volume of 100 mL with water. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, method blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed or 5% and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source. Refer to Chapter One for the proper protocol.

8.6 The method of standard addition shall be used for the analysis of all EP extracts. See Method 7000, Step 8.7, for further information.

9.0 METHOD PERFORMANCE

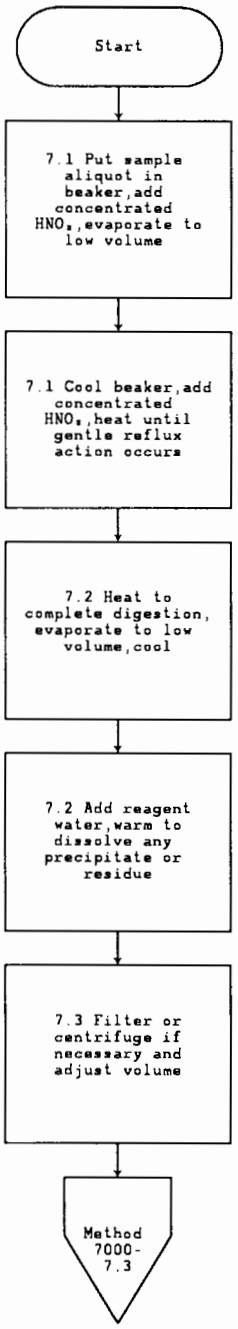
9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 3020A
ACID DIGESTION FOR AQUEOUS SAMPLES AND EXTRACTS
FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY



METHOD 3031

ACID DIGESTION OF OILS FOR METALS
ANALYSIS BY ATOMIC ABSORPTION OR ICP SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure for analysis of oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for the sixteen toxic elements listed below:

Antimony	Arsenic	Barium	Beryllium
Cadmium	Chromium	Cobalt	Copper
Lead	Molybdenum	Nickel	Selenium
Silver	Thallium	Vanadium	Zinc

Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrix of interest, at the concentration levels of interest (see Section 8.0). The resulting digestate can be analyzed by either flame atomic absorption spectrometry (FLAA), graphite furnace atomic absorption spectrometry (GFAA), or inductively coupled plasma atomic emission spectrometry (ICP-AES).

1.2 The large concentration of manganese present in the digestate of Method 3031 can interfere with the determination of low concentrations of arsenic which is important for the recycled oil regulations. As an optional step, manganese may be removed from the digestate by forming a manganese phosphate precipitate. The remaining liquid can be analyzed by either flame atomic absorption spectrometry (FLAA) or inductively coupled plasma (ICP-AES). Chlorides can be removed by the use of nitric acid for analysis by graphite furnace atomic absorption spectrometry (GFAA) for arsenic. These clean-up procedures may be applicable to other elements as can be demonstrated by appropriate procedures (Sec. 7.11).

2.0 SUMMARY OF METHOD

2.1 A representative 0.5 g sample is mixed with 0.5 g of finely ground potassium permanganate and then 1.0 mL of concentrated sulfuric acid is added while stirring. A strong exothermic reaction occurs. The sample is then treated with 2 mL concentrated nitric acid. 10 mL of concentrated HCl is added and the sample is heated until the reaction is complete and is then filtered. The filter is washed with hot concentrated HCl. The filter paper is transferred to a digestion flask, treated with 5 mL of concentrated hydrochloric acid. The sample is brought to volume and analyzed by ICP-AES or FLAA.

WARNING: THIS PROCEDURE SHOULD NOT BE ATTEMPTED BY INEXPERIENCED PERSONNEL. MANY OF THE REACTIONS ARE STRONGLY EXOTHERMIC AND CAN RESULT IN SPLATTERING OR IN THE GENERATION OF GASES. GLOVES, FACESHIELDS, AND LAB COATS MUST BE WORN WHEN WORKING WITH ACIDS. IT IS STRONGLY RECOMMENDED THAT THE ADDITION OF SULFURIC ACID BE PERFORMED BEHIND A GLASS SHIELD OR SASH.

2.2 To remove the manganese, the digestate is neutralized with concentrated ammonium hydroxide. Water and ammonium phosphate are added and the digestate is stirred while a precipitate of manganese ammonium phosphate is formed. When the precipitation is complete,

the digestate is filtered. The ammonia is then boiled off. The sample is brought to volume and analyzed on either ICP-AES or FLAA. For GFAA analysis, the volume is reduced and allowed to cool. Concentrated HNO_3 is added and the solution is heated. When the reaction is complete, bring to volume and analyze by GFAA.

3.0 INTERFERENCES

3.1 Most grades of potassium permanganate have elemental impurities that will interfere with the analysis. It is important that the permanganate be checked for purity. Background correction setting on an ICP-AES that are appropriate to the digestates of other matrices will not be effective for the digestates of oils. Background correction settings must be chosen for this unique digestate. These digestates can have very high dissolved solids, which may necessitate the use of internal standards, dilutions, or method of standard addition. Manganese is a very strong emitter and has many analytical lines. Analytical wavelengths must be chosen with care to avoid or minimize spectral overlap. Inter-element correction for manganese can be used for those instruments with that capability.

3.2 Excess ammonium hydroxide will result in the solubilization of some manganese.

3.3 To ensure comparable viscosities and chemistries between samples and standards, all standards must be matrix matched to the respective digestates.

4.0 APPARATUS AND MATERIALS

4.1 Beakers - 250 mL, or equivalent.

4.2 Temperature sensing device, e.g. thermometer, thermistor, thermocouple, or equivalent, capable of measuring temperatures between 0 and 150°C.

4.3 Filter paper - Whatman No. 41, or equivalent.

4.4 Funnels - polypropylene, or equivalent.

4.5 Heating device, e.g. hot plate, heating block, microwave or equivalent.

4.6 Volumetric flasks, of suitable precision and accuracy.

4.7 Volumetric pipettes, of suitable precision and accuracy.

4.8 Stirring device, e.g. magnetic stirrer, glass rod or equivalent.

NOTE: All glassware should be acid washed.

5.0 REAGENTS

5.1 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One of SW-846 for a definition of reagent water.

5.2 Nitric acid, concentrated, reagent grade (conc. HNO_3). Acid should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

5.3 Hydrochloric acid, concentrated, reagent grade (conc. HCl). Acid should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

5.4 Sulfuric acid, concentrated, reagent grade (conc. H_2SO_4). Acid should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

5.5 Potassium permanganate - Ultra-pure grade. Reagent should be analyzed to determine level of impurities. If method blank is < MDL, then the reagent can be used.

5.6 Organometallic standards - scandium and/or yttrium may be used as internal standards for most samples. Standards traceable to NIST Standard No. 1085, for wear metals in oil, may be used.

5.7 Base oil, analyte-free. Oil should be analyzed to determine level of impurities. If method blank is < MDL, then the reagent can be used.

5.8 Ammonium hydroxide, concentrated, reagent grade - Reagent should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

5.9 Ammonium phosphate, reagent grade - Reagent should be analyzed to determine level of impurities. If method blank is < MDL, then the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be pre-washed with detergents, acids, and water. See Chapter Three, Section 3.1.3, for further information.

6.3 Samples should be digested as soon as possible after arrival. Digestates may be kept for a period of 180 days in the case of most metals. See holding time table (Chapter Three) for specific metals of interest.

7.0 PROCEDURES

7.1 Homogenize sample and then take a representative sample of 0.5 g (± 0.01 g) and place in a beaker. Larger or smaller sample sizes can be used if needed.

> NOTE: Alternatively, with appropriate oils, H_2SO_4 and H_2O_2 may be used in repetition, with adjustments for stoichiometry, to permit the decomposition and reduce the dissolved solids content of digestate materials. If using an alternative reagent combination, equivalent performance must be demonstrated.

7.2 Add 0.5 g of potassium permanganate powder. If larger sample sizes are used, increase the amount of potassium permanganate so that the ratio of oil to potassium permanganate is still 1:1. Mix the oil and permanganate thoroughly until homogeneous. Thick oils and tars that cannot be mixed should be heated to achieve mixing (the oil may react mildly). It is important to record the amount of potassium permanganate used for each sample if analysis is by ICP-AES and correction is to be made for the amount of manganese.

If more than 10% of the sample is aromatic material, such as xylene, then the reaction will be incomplete. If this is the case, increase the amount of potassium permanganate. If the sample is a mixture of oil and other non-organic materials, reduce the amount of potassium permanganate.

NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. This should include face shields and latex gloves.

7.3 Add 1.0 mL of concentrated H_2SO_4, and stir with an appropriate stirring device. If larger sample sizes are used, increase the volume of sulfuric acid so that ratio of oil to sulfuric acid is 1 g to 2 mL. The H_2SO_4 can be added dropwise or all at once, depending on analytical needs. (Generally, dropwise is preferred when low reporting limits are needed.)

NOTE: To prevent a strong exothermic reaction, H_2SO_4 should be added dropwise to all samples unfamiliar to the analyst and to all samples that are known to be highly reactive.

The reaction can take several seconds to begin, but when it occurs it will be very quick, vigorous, and exothermic. Generally larger sample sizes will react faster than smaller. Likewise, lower average molecular weight materials will react faster than heavier. Do not be mislead by an initial lack of reactivity. A grey-white vapor will be ejected from the beaker (SO_3) and splattering and bubbling can occur. The beaker will become very hot. This step is complete when no more gases are given off and the sample should be a thick black lumpy paste. Allow the beaker to cool as needed.

NOTE: Care must be taken when working with very light organic materials, such as diesel fuels, as they may flash. Generally, the lower the average molecular weight of the material correlates to a greater danger of flashing. The danger of flashing is reduced by adding the sulfuric acid dropwise.

NOTE: If more than 10% of the sample is aromatic material, such as xylene, only a little grey-white vapor will form. this will reduce accuracy and complicate nebulization. If there is a significant amount of non-hydrocarbon material, a sputtering reaction will occur and black MnO_2 particulates will be given off. See Section 7.2.

7.4 Add 2 mL of concentrated HNO_3 and stir. This reaction will be slightly exothermic. If larger sample sizes are used, it is not always necessary to increase the volume of HNO_3 proportionately, depending on analytical needs. Some reddish-brown vapor (NO_2) may be given off. Allow the reaction to continue until complete, that is when the digestate no longer gives off fumes. Allow the beaker to cool as needed.

7.5 Add 10 mL of concentrated HCl and stir. If larger sample sizes are used, it is not always necessary to increase the volume of HCl proportionately, depending on analytical needs. This reaction will be slightly exothermic and gas formation and foaming will occur. Lighter oils will foam more than will heavier oils. If excess foaming occurs, add water to prevent sample loss. Allow the beaker to cool as needed.

7.6 Heat the beaker until there is no further gas evolution. (temperature should not exceed 150° C to prevent volatilization). There may be additional foaming or other milder reactions which may result in overflow from the beaker. If excess foaming occurs, either remove the beaker from the heating source until foaming subsides or add sufficient water to prevent overflow. The final digestate should be a clear yellow liquid with black or dark reddish-brown particulates.

7.7 Filter the digestate through Whatman 41 filter paper and collect filtrate in a volumetric flask or beaker.

7.8 Wash the digestion beaker and filter paper, while still in the funnel, with no more than 5 mL of hot HCl.

NOTE: The purpose of this next step is to recover antimony, barium, and silver that may not have been complete solubilized. If the sample is not being prepared for these analytes, the next step may be skipped.

7.9 (Optional) After having washed the filter paper, remove the filter and residue from the funnel and place in back in the beaker. Add 5 mL of conc. HCl and place the beaker back on the heating source until the filter paper dissolves (temperature should not exceed 150°C ± 5°C to prevent volatilization). Remove the beaker from the heating source and wash the cover and sides with reagent grade water and then filter the residue and collect the filtrate in the same flask or beaker as in Sections 7.6 and 7.7. Allow the filtrate to cool and quantitatively transfer to a volumetric flask. Bring to volume.

7.10 (Optional) If the filtrate is collected in a beaker, the filtrate can be heated again to drive off excess HCl. This can reduce matrix effects in sample introduction (temperature should not exceed 150°C ± 5°C to prevent volatilization). When sufficient HCl has been removed, remove the beaker from the heating source, allow to cool, and then transfer the contents to a volumetric flask and bring to volume. However, if too much HCl is removed, barium, silver and antimony can be lost.

7.11 Analyze the filtrate by either ICP-AES or FLAA. Depending on the final volume selected, the total solids in the digestate may be high enough to cause nebulization problems. Problems due to high dissolved solids may be corrected by 1) following optional Section 7.9, 2) using internal standards, 3) using Flow Injection Analysis, or 4) using other matrix correction procedures.

Manganese Removal Steps

NOTE: The purpose of these next steps is to remove the manganese in the digest by precipitating it as manganese ammonium phosphate under alkaline conditions. Elements that do not form insoluble phosphates, such as arsenic, are filtered out and can be analyzed at lower concentrations.

7.12 Take the digestate, or portion of digestate and reduce the volume to remove as much HCl as possible without going below 10 mL. Then add conc. NH_4OH until pH is 7 or greater. For most matrices, the digestate will change colors (often from yellow to brown) at pH 7. A mild exothermic reaction will occur immediately.

7.13 Add at least 2 g ammonium phosphate for each 1 g of potassium permanganate used in the digestion and stir. An excess of phosphate is needed for good analyte recovery. Then add enough water and mix to ensure maximum precipitation. A pink or yellow silky amorphous precipitate, manganese ammonium phosphate, will form. If too much NH_4OH is used some of the manganese ammonium phosphate can be solubilized. Stir until precipitation is complete. Some ammonium phosphate may remain unreacted at the bottom of the beaker.

7.14 Filter the digestate through Whatman 41 filter paper (or equivalent) and collect filtrate in a volumetric flask or beaker.

7.15 Heat the filtrate to volatilize the ammonia (temperature should not exceed 150°C ± 5°C to prevent volatilization). the volume of filtrate can be reduced by heating to no less than 10 mL. If too much water is removed any ammonium chloride formed will solidify. If this occurs, either add enough water to dissolve the solids or filter out the solids and wash the residue with deionized water. A third alternative is to use nitric acid to destroy the ammonium chloride by using the step in Section 7.17.

7.16 The filtrate can be analyzed by ICP-AES or FLAA. The chlorides in the digestate will prevent the analysis by GFAA.

7.17 To analyze the digestate by GFAA, reduce the volume as much as possible. Cool and add sufficient conc. HNO_3 to drive off all chlorides. Heat gently and a mild exothermic reaction will occur. When no more reddish-brown gas (NO_2) is given off, the reaction is complete and the digestate can be cooled and taken to volume. This liquid can be analyzed by ICP-AES, FLAA, or GFAA.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, method blanks should be carried throughout the entire sample-preparation and analytical process. The blank will be useful in determining if samples are being contaminated. Do not subtract measured blank values from sample results. Use blanks to determine the source of contamination and eliminate it.

NOTE: This blank MUST include an analyte-free oil or explosive reactions can occur.

8.3 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Refer to Chapter One for the proper protocol.

8.4 Organometallic standard reference materials (SRMs) or laboratory control samples spiked with organo-metallic standards should be employed to determine accuracy. Recoveries of SRMs and/or spikes should be +/- 25% of their true values.

9.0 METHOD PERFORMANCE

Refer to Tables 1, 2, 3, and 4.

10.0 REFERENCES

1. HMU 800, Acid Digestion of Oils for Metals Analysis by FLAA or ICP Spectroscopy, Southern California Laboratories.

TABLE 1
PERFORMANCE DATA USING SRM 1085[a]

Element	True Value (ppm)	Mean Value (ppm)	Percent Recovery	Standard Deviation (ppm)
Silver	306	283	92	35
Chromium	296	295	100	14
Copper	295	291	99	11
Molybdenum	303	283	93	23
Nickel	303	261	86	8.6
Lead	297	297	100	17
Vanadium	292	393	135	12

[a] n = 5

TABLE 2
PERCENT RECOVERIES AND STANDARD DEVIATIONS[ab]

Analyte	Method of Analysis	True Value (ppm)	Mean Value (ppm)	Percent Recovery	Standard Deviation (ppm)
Silver	ICP-AES	306	302	98	22
Silver	FLAA	306	254	83	6.7
Chromium	ICP-AES	296	278	94	19
Chromium	FLAA	296	240	81	16
Copper	ICP-AES	295	301	102	24
Copper	FLAA	295	250	85	11
Molybdenum	ICP-AES	303	282	93	12
Nickel	ICP-AES	303	262	86	24
Nickel	FLAA	303	237	78	9.3
Lead	ICP-AES	297	246	83	17
Lead	FLAA	297	260	88	4.2
Vanadium	ICP-AES	292	292	100	14

[a] Procedures tested using NIST SRM 1085.
[b] n = 12

TABLE 3
MEAN MEASURED VALUES FOR OIL STANDARDS BY SIMULTANEOUS ICP-AES[a]

Analyte	Concentration (µg/g) 500	100	50	25	5.0	2.5
Silver	472	90.2	46.2	23.1	5.15 (1)[b]	2.3 (1)[b]
Arsenic	146	67.9	39.0	18.1	1.8 (1)[b]	<1
Barium	31.0	26.6	8.4	5.8	4.67	2.17
Beryllium	575	113	56.6	28.2	6.26	3.25
Cadmium	442	83.5	43.87	21.6	3.96	1.67
Cobalt	441	82.3	42.4	20.7	3.36	0.69
Chromium	487	95.2	50.5	27.6	10.1	7.09
Copper	566	114	55.6	25.5	3.11	0.50
Molybdenum	529	95.7	48.7	26.1	6.47	3.64
Nickel	458	86.4	46.4	25.1	5.19	4.80
Lead	360	62.0	30.3	16.1	3.34	3.05
Antimony	667[c]	84.3	68.3	42.3	20.4	7.22
Selenium	350	93.0	50.1	25.8	11.8	11.6
Thallium	NA	72.2	37.6	28.1	10.9	<1
Vanadium	512	98.2	49.8	27.6	13.6	7.88
Zinc	512	93.2	43.8	16.8	1.6	<1

[a] n = 8
[b] Numbers in parenthesis represent the number of "less than" values.
[c] The highest standard for antimony was 1000 µg/g.

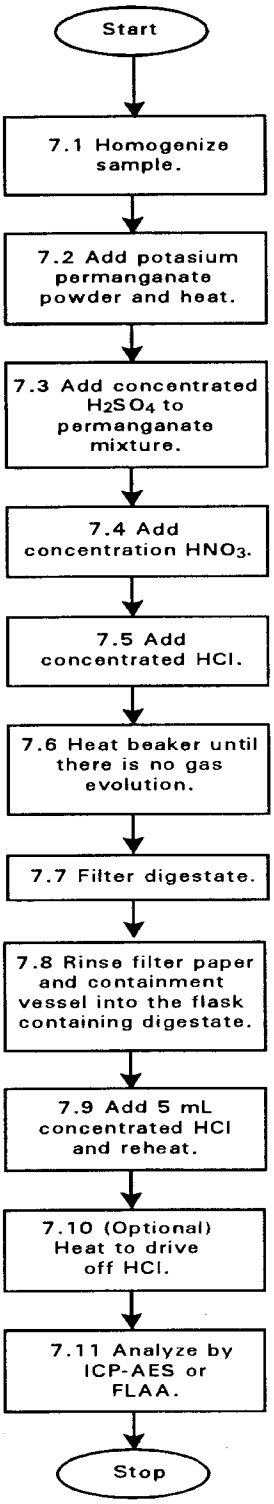
NA = Not Analyzed

TABLE 4
STANDARD DEVIATIONS FOR OIL STANDARDS BY SIMULTANEOUS ICP-AES

Analyte	Concentration (µg/g) 500	100	50	25	5.0	2.5
Silver	14	3.6	1.1	4.1	6.3	0.46
Arsenic	3.1	4.1	1.7	1.9	1.1	[b]
Barium	0.88	9.2	4.0	5.9	0.30	0.18
Beryllium	3.4	1.5	1.5	0.41	0.35	0.46
Cadmium	2.1	1.7	0.73	0.66	0.53	0.26
Cobalt	2.1	1.8	0.69	1.3	0.24	0.30
Chromium	2.6	6.5	1.3	4.0	4.5	5.1
Copper	3.3	2.2	1.9	1.2	1.7	[b]
Molybdenum	3.2	1.6	0.62	1.0	0.69	0.36
Nickel	2.3	2.6	0.08	7.5	1.2	2.0
Lead	1.5	9.8	5.6	2.4	1.6	3.5
Antimony	34[c]	2.5	1.6	2.7	3.7	1.7
Selenium	5.7	5.4	6.8	8.0	6.4	4.3
Thallium	NA	8.5	13	18	8.2	[b]
Vanadium	3.8	4.4	0.84	7.2	11	8.3
Zinc	2.4	2.8	3.0	3.2	4.7	[b]

[a] n = 5
[b] The results were non-detects.
[c] The highest antimony standard was 1000 µg/g.

NA = Not Analyzed


Start
7.1 Homogenize sample.
7.2 Add potasium permanganate powder and heat.
7.3 Add concentrated H_2SO_4 to permanganate mixture.
7.4 Add concentration HNO_3.
7.5 Add concentrated HCl.
7.6 Heat beaker until there is no gas evolution.
7.7 Filter digestate.
7.8 Rinse filter paper and containment vessel into the flask containing digestate.
7.9 Add 5 mL concentrated HCl and reheat.
7.10 (Optional) Heat to drive off HCl.
7.11 Analyze by ICP-AES or FLAA.
Stop

METHOD 3040A

DISSOLUTION PROCEDURE FOR OILS, GREASES, OR WAXES

1.0 SCOPE AND APPLICATION

1.1 This method is used for the preparation of samples containing oils, greases, or waxes for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) for the following metals:

Antimony	Copper
Arsenic	Iron
Barium	Lead
Beryllium	Manganese
Cadmium	Nickel
Chromium	Vanadium

1.2 This method is a solvent dissolution procedure, not a digestion procedure. This procedure can be very useful in the analysis of crude oil, but with spent or used oil high in particulate material it is less effective; most particulate material is not dissolved, and therefore the analysis is not a "total" metal determination. Because the highest percentage of metals is expected to be contained in the particulate material, oil analysis using Method 3040A will not provide an adequate estimate of the total metals concentration.

Caution: Overheating of oils and solvents can result in an explosion or fire, caution should be taken.

1.3 This method is applicable for the dissolution of multi-phasic aqueous wastes containing either oils, greases, or waxes. If a waste is multi-phasic it can be determined by using Method 3040A in combination with one of the other sample preparation methods.

Caution: The analysis of solvents in an ICP-AES should only be conducted after consultation with the manufacturer.

1.4 This method is suitable for conducting analyses in support of TCLP determinations if the percent solids, as conducted according to the procedures specified in the Method 1311, are below 0.5%.

2.0 SUMMARY OF METHOD

2.1 A representative sample is dissolved in an appropriate solvent (e.g., xylene, kerosene, or methyl isobutyl ketone). Organometallic standards are prepared using the same solvent, and the samples and standards are analyzed by FLAA or ICP-AES.

3.0 INTERFERENCES

3.1 Diluted samples and diluted organometallic standards are often unstable. Once standards and samples are diluted, they should be analyzed as soon as possible.

3.2 Solvent blanks should be used to rinse nebulizers thoroughly following aspiration of high concentration standards or samples.

3.3 Viscosity differences can result in different rates of sample introduction; therefore, all analyses shall be performed by the method of standard addition or internal standardization (only for ICP-AES). Peristaltic pumps often prove useful when analysis is performed by ICP-AES. In addition, a mass-flow controller may also alleviate some viscosity problems.

4.0 APPARATUS AND MATERIALS

4.1 Volumetric glassware or equivalent.

4.2 Analytical balance, 300 g capacity, minimum $\pm$ 0.01g.

4.3 Atomic absorption spectrometer: With an auxiliary oxidant control and a mechanism for background correction.

4.4 Inductively coupled plasma emission spectrometer system: With a mechanism for background correction and interelement interference correction. A peristaltic pump is optional.

5.0 REAGENTS

5.1 Methyl isobutyl ketone (MIBK).

5.2 Xylene.

5.3 Kerosene.

5.4 Organometallic standards - scandium and yttrium may be used as internal standards for most samples. Standards traceable to NIST Standard No. 1085, for wear metals in oil, may be used. (Two possible sources are Conostan Division, Conoco Speciality Products, Inc., P.O. Box 1267, Ponca City, OK 74601, and the U.S. Department of Commerce, National Institutes of Standards and Technology, Washington, DC 20234).

5.5 Base Oil.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples shall be stored in an undiluted state at room temperature.

6.3 Samples should be processed and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Weigh out a 2 gram representative sample of the waste or extract. Separate and weigh the phases if more than one phase is present.

7.2 Internal standards should be added to all samples at the mid-point of the concentration range, prior to dilution (the internal standard concentration may vary depending on your instrument or instrument configuration). Weigh an aliquot of the organic phase and dilute the aliquot in the appropriate solvent. Warming facilitates the subsampling of crude-type oils and greases and wax-type wastes. Xylene or kerosene are usually the preferred solvent for longer-chain hydrocarbons and for most analyses performed by ICP-AES. The longer-chain hydrocarbons usually require a minimum of a 1:10 (W/W) dilution, and lighter oils may require only a 1:5 (W/W) dilution if low detection limits are required.

7.3 Prepare a series of standards using the base oil and diluting by the same factor used for the samples. Add the internal standard before diluting. The concentration of the internal standard should be in the middle of the concentration range (The internal standard concentration may vary depending on your instrument or instrument configuration).

7.4 If the sample contains particulates, the result may be variable depending on whether the particles are aspirated into the instrument. Samples may be centrifuged after dilution to remove particulates from the solution prior to analysis.

7.5 All metals must be analyzed by the method of standard additions if an internal standard is not used. Because the method of standard additions can account only for multiplicative interferences (matrix or physical interferences), the analytical program must account for additive interference (nonspecific absorption and scattering in FLAA and nonspecific emission and interelement interference in ICP-AES) by employing background correction when using the ICP-AES.

7.6 Sample preparation for the method of standard additions can be performed on a weight or volume basis. Sample aliquots of viscous wastes should be weighed. Weigh identical amounts of the sample into three wide-mouth vials. Dilute the first vial such that the final concentration falls on the lower end of the linear portion of the calibration curve and significantly above the detection limit. Add sufficient standard to the second aliquot to increase the sample concentration by approximately 50%. Adjust the third sample concentration so that it is approximately twice that of the first. The second and third aliquots are then diluted to the same final volume as the first aliquot. Because of the wide variability in waste samples, and the problems encountered with analyzing them, the analyst's best judgement must be used to permit efficient use of this method.

7.7 Set up and calibrate the analytical instrumentation according to the manufacturer's directions for nonaqueous samples.

7.8 Report data as the weighted average for all sample phases.

$$[(P_1 \times C_1) + (P_2 \times C_2)]/P_T = C_F$$

P_1 = weight of the first phase (kg)

P_2 = weight of the second phase (kg)

C_1 = concentration of the first phase (mg/kg)

C_2 = concentration of the second phase (mg/kg)

P_T = weight of both phases (kg)

C_F = final concentration of waste (mg/kg)

7.9 For nonaqueous TCLP extracts and other samples where results are reported in "mg/L" units, the conversion from "mg/kg" to "mg/L" units can be done by determining the density of the liquid and converting mathematically.

8.0 QUALITY CONTROL

8.1 Preparation blanks (e.g., Conostan base oil or mineral oil plus reagents) should be carried through the complete sample-preparation and analytical process on a routine basis. These blanks will be useful in detecting and determining the magnitude of any sample contamination. Refer to Chapter One.

8.2 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. Refer to Chapter One.

8.3 Samples and standards should be diluted as closely as possible to the time of analysis.

8.4 All analyses must be performed by the method of standard additions if an internal standard is not used. See Method 7000, Section 8.7, for further information.

8.5 Data must be corrected for background absorption and emission and interelement interferences.

9.0 METHOD PERFORMANCE

9.1 Refer to Tables 1 and 2 for a single lab study.

10.0 REFERENCES

1. Used Oil Characterization Sampling and Analysis Program. Draft Final Report. February 15, 1991.

TABLE 1

METHOD PERFORMANCE DATA
FROM SINGLE LAB STUDY: ASSESSMENT OF ACCURACY

ANALYTE	# ANALYSES	MEAN PERCENT SPIKE RECOVERY	STANDARD DEVIATION	OUTLIERS[a]
Arsenic	2	76	39.6	1
Cadmium	20	100.6	16.8	4
Chromium	20	107.2	13.1	2
Lead	20	97.4	20.2	2
Barium	20	97.0	30.7	4

TABLE 2

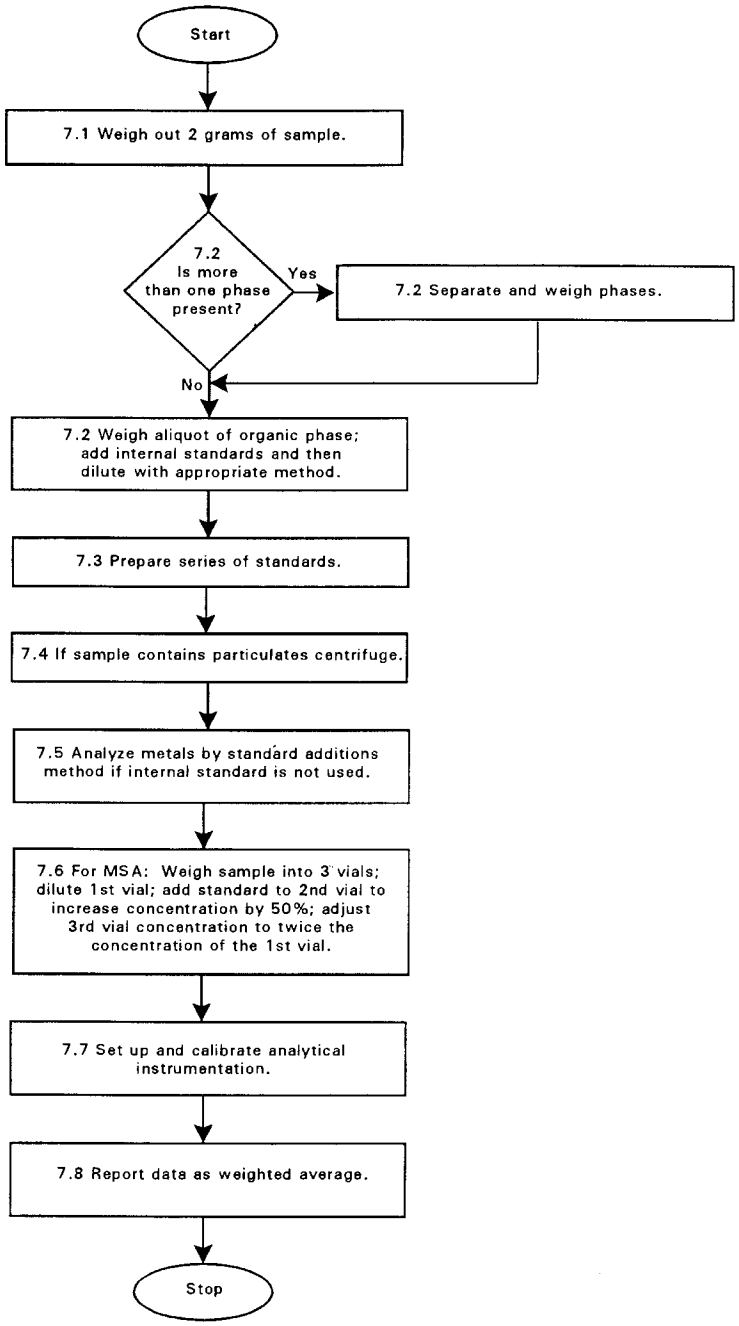
METHOD PERFORMANCE DATA
FROM SINGLE LAB STUDY: ASSESSMENT OF PRECISION

ANALYTE	# REPLICATE PAIRS	RELATIVE % DIFFERENCE	STANDARD DEVIATION	OUTLIERS[b]
Arsenic	1	73	---	1
Cadmium	10	1.8	1.9	0
Chromium	10	2.8	1.9	0
Lead	10	4.1	6.6	1
Barium	10	5.9	12.1	1

[a] Percent recovery outside of the laboratory's 80 - 120 % acceptance criteria. Outliers included in statistical analysis.

[b] RPD outside of the laboratory's 20 % acceptance criteria. Outliers included in statistical analysis.

METHOD 3040A
DISSOLUTION PROCEDURE FOR OILS, GREASES, OR WAXES



METHOD 3050B

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method has been written to provide two separate digestion procedures, one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis of samples by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by this method may be analyzed by ICP-AES or GFAA for all the listed metals as long as the detecion limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest (See Section 8.0). The recommended determinative techniques for each element are listed below:

FLAA/ICP-AES		GFAA/ICP-MS
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		
Vanadium		

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become “environmentally available.” By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2).

2.2 For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.

2.3 For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals (see Section 7.3.1: NOTE), this digestate is filtered and the filter paper and residues are rinsed, first

with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.4 If required, a separate sample aliquot shall be dried for a total percent solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Sec. 8.0 to aid in determining whether Method 3050B is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Digestion Vessels - 250-mL.

4.2 Vapor recovery device (e.g., ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system).

4.3 Drying ovens - able to maintain 30°C ± 4°C.

4.4 Temperature measurement device capable of measuring to at least 125°C with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical balance - capable of accurate weighings to 0.01 g.

4.8 Heating source - Adjustable and able to maintain a temperature of 90-95°C. (e.g., hot plate, block digestor, microwave, etc.)

4.9 Funnel or equivalent.

4.10 Graduated cylinder or equivalent volume measuring device.

4.11 Volumetric Flasks - 100-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.5 Hydrogen peroxide (30%), H_2O_2. Oxidant should be analyzed to determine level of impurities. If method blank is < MDL, the peroxide can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqueous samples should be refrigerated upon receipt and analyzed as soon as possible.

6.4 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned according to the guidance in Sec. 6.0 to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

> NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

7.2 For the digestion of samples for analysis by GFAA or ICP-MS, add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass or vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a ribbed watch glass or vapor recovery system, either allow the solution to evaporate to approximately 5 mL without boiling or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by GFAA or ICP-MS by adding 10 mL of 1:1 HNO_3, mixing the slurry and then covering with a vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C without boiling. Allow the sample to cool for 5 minutes, add 5 mL of concentrated HNO_3, heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL concentrated HNO_3) until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a vapor recovery system, heat the sample to 95°C ± 5°C and reflux for 10 minutes at 95°C ± 5°C without boiling.

7.2.1 After the step in Section 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the vessel with a watch glass or vapor recovery device and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel.

NOTE: Alternatively, for direct energy coupled devices: After the Sec. 7.2 "NOTE" step has been completed and the sample has cooled for 5 minutes, add slowly 10 mL of 30% H_2O_2. Care must be taken to ensure that losses do not occur due to excessive vigorous effervesence. Go to Section 7.2.3.

7.2.2 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.2.3 Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95°C ± 5°C in 6 minutes and remain at 95°C ± 5°C without boiling for 10 minutes.

7.2.4 After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by GFAA or ICP-MS.

7.2.4.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.2.4.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.2.4.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier.

7.3 For the analysis of samples for FLAA or ICP-AES, add 10 mL conc. HCl to the sample digest from 7.2.3 and cover with a watch glass or vapor recovery device. Place the sample on/in the heating source and reflux at 95°C ± 5°C for 15 minutes.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by FLAA and ICP-AES by adding 5 mL HCl and 10 mL H_2O to the sample digest from 7.2.3 and heat the sample to 95°C ± 5°C, Reflux at 95°C ± 5°C without boiling for 5 minutes.

7.4 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Make to volume and analyze by FLAA or ICP-AES.

NOTE: Section 7.5 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.

7.5 Add 2.5 mL conc. HNO_3 and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.

7.5.1 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask.

7.5.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

7.5.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by FLAA or ICP-AES.

7.6 Calculations

7.6.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.6.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process according to the frequency described in Chapter One. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing method blanks.

8.3 Spiked duplicate samples should be processed on a routine basis and whenever a new sample matrix is being analyzed. Spiked duplicate samples will be used to determine precision and bias. The criteria of the determinative method will dictate frequency, but 5% (one per batch) is recommended or whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spiked replicates.

8.4 Limitations for the FLAA and ICP-AES optional digestion procedure. Analysts should be aware that the upper linear range for silver, barium, lead, and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded. The approximate linear upper ranges for a 2 gram sample size:

Ag	2,000 mg/kg
As	1,000,000 mg/kg
Ba	2,500 mg/kg
Be	1,000,000 mg/kg
Cd	1,000,000 mg/kg
Co	1,000,000 mg/kg
Cr	1,000,000 mg/kg
Cu	1,000,000 mg/kg
Mo	1,000,000 mg/kg
Ni	1,000,000 mg/kg
Pb	200,000 mg/kg
Sb	200,000 mg/kg
Se	1,000,000 mg/kg
Tl	1,000,000 mg/kg
V	1,000,000 mg/kg
Zn	1,000,000 mg/kg

NOTE: These ranges will vary with sample matrix, molecular form, and size.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the recoveries of the three matrices presented in Table 2 were obtained using the digestion procedure outlined for samples prior to analysis by FLAA and ICP-AES. The spiked samples were analyzed in duplicate. Tables 3-5 represents results of analysis of NIST Standard Reference Materials that were obtained using both atmospheric pressure microwave digestion techniques and hot-plate digestion procedures.

10.0 REFERENCES

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TABLE 1

STANDARD RECOVERY (%) COMPARISON FOR
METHODS 3050A AND 3050B[a]

Analyte	METHOD 3050A[a]	METHOD 3050B w/option[a]
Ag	9.5	98
As	86	102
Ba	97	103
Be	96	102
Cd	101	99
Co	99	105
Cr	98	94
Cu	87	94
Mo	97	96
Ni	98	92
Pb	97	95
Sb	87	88
Se	94	91
Tl	96	96
V	93	103
Zn	99	95

[a] All values are percent recovery. Samples: 4 mL of 100 mg/mL multistandard; n = 3.

TABLE 2

PERCENT RECOVERY COMPARISON FOR METHODS 3050A AND 3050B

Analyte	Percent Recovery[a,c]							
	Sample 4435		Sample 4766		Sample HJ		Average	
	3050A	3050B	3050A	3050B	3050A	3050B	3050A	3050B
Ag	9.8	103	15	89	56	93	27	95
As	70	102	80	95	83	102	77	100
Ba	85	94	78	95	b	b	81	94
Be	94	102	108	98	99	94	99	97
Cd	92	88	91	95	95	97	93	94
Co	90	94	87	95	89	93	89	94
Cr	90	95	89	94	72	101	83	97
Cu	81	88	85	87	70	106	77	94
Mo	79	92	83	98	87	103	83	98
Ni	88	93	93	100	87	101	92	98
Pb	82	92	80	91	77	91	81	91
Sb	28	84	23	77	46	76	32	79
Se	84	89	81	96	99	96	85	94
Tl	88	87	69	95	66	67	74	83
V	84	97	86	96	90	88	87	93
Zn	96	106	78	75	b	b	87	99

a - Samples: 4 mL of 100 mg/mL multi-standard in 2 g of sample. Each value is percent recovery and is the average of duplicate spikes.

b - Unable to accurately quantitate due to high background values.

c - Method 3050B using optional section.

Table 3
Results of Analysis of Nist Standard Reference Material 2704
"River Sediment" Using Method 3050B (µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	101 ± 7	89 ± 1	98 ± 1.4	100 ± 2	98.6 ± 5.0
Pb	160 ± 2	145 ± 6	145 ± 7	146 ± 1	161 ± 17
Zn	427 ± 2	411 ± 3	405 ± 14	427 ± 5	438 ± 12
Cd	NA	3.5 ± 0.66	3.7 ± 0.9	NA	3.45 ± 0.22
Cr	82 ± 3	79 ± 2	85 ± 4	89 ± 1	135 ± 5
Ni	42 ± 1	36 ± 1	38 ± 4	44 ± 2	44.1 ± 3.0

NA - Not Available

Table 4
Results of Analysis of NIST Standard Reference Material 2710
"Montana Soil (Highly Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

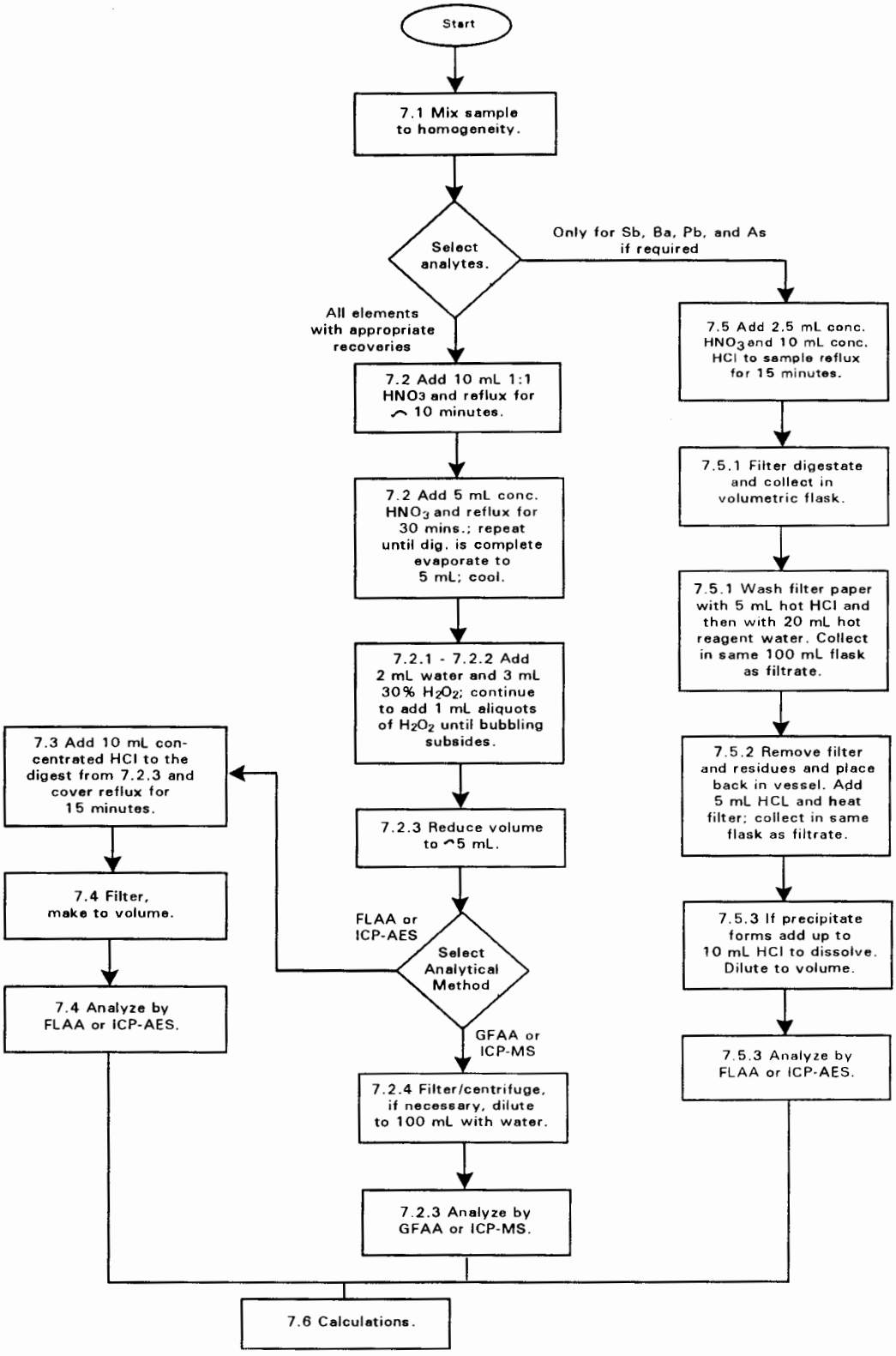
Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	2640 ± 60	2790 ± 41	2480 ± 33	2910 ± 59	2700	2950 ± 130
Pb	5640 ± 117	5430 ± 72	5170 ± 34	5720 ± 280	5100	5532 ± 80
Zn	6410 ± 74	5810 ± 34	6130 ± 27	6230 ± 115	5900	6952 ± 91
Cd	NA	20.3 ± 1.4	20.2 ± 0.4	NA	20	21.8 ± 0.2
Cr	20 ± 1.6	19 ± 2	18 ± 2.4	23 ± 0.5	19	39*
Ni	7.8 ± 0.29	10 ± 1	9.1 ± 1.1	7 ± 0.44	10.1	14.3 ± 1.0

NA - Not Available * Non-certified values, for information only.

Table 5
Results of Analysis of NIST Standard Reference Material 2711
"Montana Soil (Moderately Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	107 ± 4.6	98 ± 5	98 ± 3.8	111 ± 6.4	100	114 ± 2
Pb	1240 ± 68	1130 ± 20	1120 ± 29	1240 ± 38	1100	1162 ± 31
Zn	330 ± 17	312 ± 2	307 ± 12	340 ± 13	310	350.4 ± 4.8
Cd	NA	39.6 ± 3.9	40.9 ± 1.9	NA	40	41.7 ± 0.25
Cr	22 ± 0.35	21 ± 1	15 ± 1.1	23 ± 0.9	20	47*
Ni	15 ± 0.2	17 ± 2	15 ± 1.6	16 ± 0.4	16	20.6 ± 1.1

NA - Not Available
* Non-certified values, for information only.


Start
7.1 Mix sample to homogeneity.
Select analytes.
Only for Sb, Ba, Pb, and As if required
All elements with appropriate recoveries
7.2 Add 10 mL 1:1 HNO3 and reflux for ~ 10 minutes.
7.2 Add 5 mL conc. HNO3 and reflux for 30 mins.; repeat until dig. is complete evaporate to 5 mL; cool.
7.2.1 - 7.2.2 Add 2 mL water and 3 mL 30% H2O2; continue to add 1 mL aliquots of H2O2 until bubbling subsides.
7.2.3 Reduce volume to ~5 mL.
FLAA or ICP-AES
Select Analytical Method
GFAA or ICP-MS
7.2.4 Filter/centrifuge, if necessary, dilute to 100 mL with water.
7.2.3 Analyze by GFAA or ICP-MS.
7.3 Add 10 mL concentrated HCl to the digest from 7.2.3 and cover reflux for 15 minutes.
7.4 Filter, make to volume.
7.4 Analyze by FLAA or ICP-AES.
7.5 Add 2.5 mL conc. HNO3 and 10 mL conc. HCl to sample reflux for 15 minutes.
7.5.1 Filter digestate and collect in volumetric flask.
7.5.1 Wash filter paper with 5 mL hot HCl and then with 20 mL hot reagent water. Collect in same 100 mL flask as filtrate.
7.5.2 Remove filter and residues and place back in vessel. Add 5 mL HCL and heat filter; collect in same flask as filtrate.
7.5.3 If precipitate forms add up to 10 mL HCl to dissolve. Dilute to volume.
7.5.3 Analyze by FLAA or ICP-AES.
7.6 Calculations.

METHOD 3051

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of sludges, sediments, soils, and oils for the following elements:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Mercury	Silver	Zinc
Beryllium				

1.2 This method is provided as an alternative to Method 3050. It is intended to provide a rapid multielement acid leach digestion prior to analysis so that decisions can be made about site cleanup levels, the need for TCLP testing of a waste and whether a BDAT process is providing acceptable performance. If a decomposition including hydrochloric acid is required for certain elements, it is recommended that Method 3050A be used. Digests produced by the method are suitable for analysis by flame atomic absorption (FLAA), graphite furnace atomic absorption (GFAA), inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS). Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3051.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 10 mL of concentrated nitric acid for 10 min using microwave heating with a suitable laboratory microwave unit. The sample and acid are placed in a fluorocarbon (PFA or TFM) microwave vessel. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate SW-846 method (Ref. 1).

3.0 INTERFERENCES

3.1 Very reactive or volatile materials that may create high pressures when heated may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g when used in the 120 mL vessels with a pressure relief device that has an upper limit of 7.5 ± 0.7 atm (110 ± 10 psi).

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Pressure, or especially temperature, monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

> CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several signifant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vesselsequippedres, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.
>
> CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mecahnisms or containers with PFA-fluorocarbon liners and pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details consult reference 2.

CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Filter funnel, glass or disposable polypropylene.

4.5 Analytical balance, 300 g capacity, and minimum ± 0.01 g.

5.0 REAGENTS

5.1 All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.1.1 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids and water. Plastic and glass containers are both suitable. See Chapter Three, sec. 3.1.3 of this manual, for further information.

6.3 Samples must be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section

7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using athe procedure described in section 7.1.4. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2°C). One kg of reagent water is weighed (1,000.0 g $\pm$ 0.1 g) into a

fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2°C measured to ± 0.05°C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05°C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2°C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Eq. 1
$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t}$$

Where:

P = the apparent power absorbed by the sample in watts (W) (W=joule·sec^{-1})

K = the conversion factor for thermochemical calories·sec^{-1} to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat (cal·g^{-1}·$°C^{-1}$) of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g^{-1}·$°C^{-1}$) the calibration equation simplifies to:

Eq. 2
$$P = (\Delta T)\ (34.86)$$

> NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and capassembly to 0.001 g prior to use.

7.3.2 Weigh a well-mixed sample to the nearest 0.001 g into the fluorocarbon sample vessel equipped with a single-ported cap and a pressure relief valve. For soils, sediments, and sludges use no more than 0.500 g. For oils use no more than 0.250 g.

7.3.3 Add 10 ± 0.1 mL concentrated nitric acid in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lbs (16 N-m) or according to the unit manufacturer's directions. Weigh the vessels to the nearest 0.001 g. Place the vessels in the microwave carousel.

CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

CAUTION: All samples known or suspected of containing more than 5-10% organic material should be predigested in a hood for at least 15 minutes.

7.3.4 Properly place the carousel in the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. Any vessels containing 10 mL of nitric acid for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with 10 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 4). Irradiate each group of sample vessels for 10 minutes. The temperature of each sample should rise to 175 °C in less than 5.5 minutes and remain between 170-180 °C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most soil, sludge, and sediment samples (Ref. 5). The pressure will exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases the pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 atm (110 ± 10 psi). All vessels should be sealed according to the manufacturers recommended specifications.

7.3.4.1 Newer microwave units are capable of higher power (W) that permits digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different values of power as long as they result in the same time and temperature conditions defined in 7.3.4. That is, any sequence of power that brings the samples to 175°C in 5.5 minutes and permits a slow rise to 175 - 180°C during the remaining 4.5 minutes (Ref. 5).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings provided to reproduce the reaction conditions defined in 7.3.4, then these alternative vessels may be used (Ref. 1,2).

7.3.5 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of acid plus sample has decreased by more than 10 percent from the original weight, discard the sample. Determine the reason for the weight loss. These are typically attributed to loss of vessel seal integrity, use of a digestion time longer than 10 minutes, too large a sample, or improper heating conditions. Once the source of the loss has been corrected, prepare a new sample or set of samples for digestion beginning at 7.3.1.

7.3.6 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

7.3.6.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.6.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.6.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.7 Dilute the digest to a known volume ensuring that the samples and standards are matrix matched. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision: Precision data for Method 3051, as determined by the statistical examination of interlaboratory test results, is located in Tables 1 and 2.

9.2 Repeatability: If successive results are obtained by the same analyst with the same apparatus under constant operating conditions on identical test material, then the difference between these successive results will not, with 95% probability, exceed the repeatability value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.206\ x$$

in the long run, where x is one result in μg/g (Ref. 6).

9.3 Reproducibility: If two successive measurements are made independently by each of two different analysts working in different laboratories on identical test material, then the difference between the average result for each analyst will not, with 95% probability, exceed the reproducibility value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.303\ x$$

in the long run, where x is the average of two successive measurements in μg/g (Ref. 2).

As can be seen in Table 1, repeatability and reproducibility differ between elements, and usually depend on that element's concentration. Table 2 provides an example of how users of the method can determine expected values for repeatability and reproducibility; nominal values of lead have been used for this model (Ref. 6).

9.4 Bias: In the case of SRM 1085 - Wear Metals in Oil, the bias of this test method is different for each element. An estimate of bias, as shown in Table 3, is:

$$\text{Bias} = \text{Amount found} - \text{Amount expected.}$$

However, the bias estimate inherits both the uncertainty in the measurements made using Method 3051 and the uncertainty on the certificate, so whether the bias is real or only due to measurement error must also be considered. The concentrations found for Al, Cr, and Cu using Method 3051 fall within their certified ranges on SRM 1085, and 95% confidence intervals for Fe and Ni overlap with their respective certified ranges; therefore, the observed biases for these elements are probably due to chance and should be considered insignificant. Biases should not be estimated at all for Ag and Pb because these elements were not certified. Therefore, the only two elements considered in this table for which the bias estimates are significant are Mg and Mo.

10.0 REFERENCES

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7. Kingston, H. M., Walter, P. J., "Comparison of Microwave Versus Conventional Dissolution for Environmental Applications", Spectroscopy, vol. 7 No. 9,20-27,1992.

TABLE 1.
EQUATIONS RELATING REPEATABILITY AND REPRODUCIBILITY TO MEAN CONCENTRATION OF DUPLICATE DETERMINATION WITH 95 PERCENT CONFIDENCE

Element	Repeatability	Reproducibility
Ag	0.195X[a]	0.314X
Al	0.232X	0.444X
B	12.9[b]	22.6[b]
Ba	0.238X	0.421X
Be	0.082[b]	0.082[b]
Ca	0.356X	1.27X
Cd	0.385X	0.571X
Co	0.291X	0.529X
Cr	0.187X	0.195X
Cu	0.212X	0.322X
Fe	0.257X	0.348X
Mg	0.238X	0.399X
Mn	1.96X1/2[c]	4.02X1/2
Mo	0.701X	0.857X
Ni	0.212X	0.390X
Pb	0.206X	0.303X
Sr	0.283X	0.368X
V	1.03X1/2	2.23X1/2
Zn	3.82X1/2	7.69X1/2

[a]Log transformed variable based on one-way analysis of variance.
[b]Repeatability and reproducibility were independent of concentration.
[c]Square root transformed variable based on one-way analysis of variance.

TABLE 2.
REPEATABILITY AND REPRODUCIBILITY FOR LEAD
BY METHOD 3051

Average Value	Repeatability	Reproducibility
50	10.3	15.2
100	20.6	30.3
200	41.2	60.6
300	61.8	90.9
400	82.4	121
500	103	152

All results are in mg/Kg

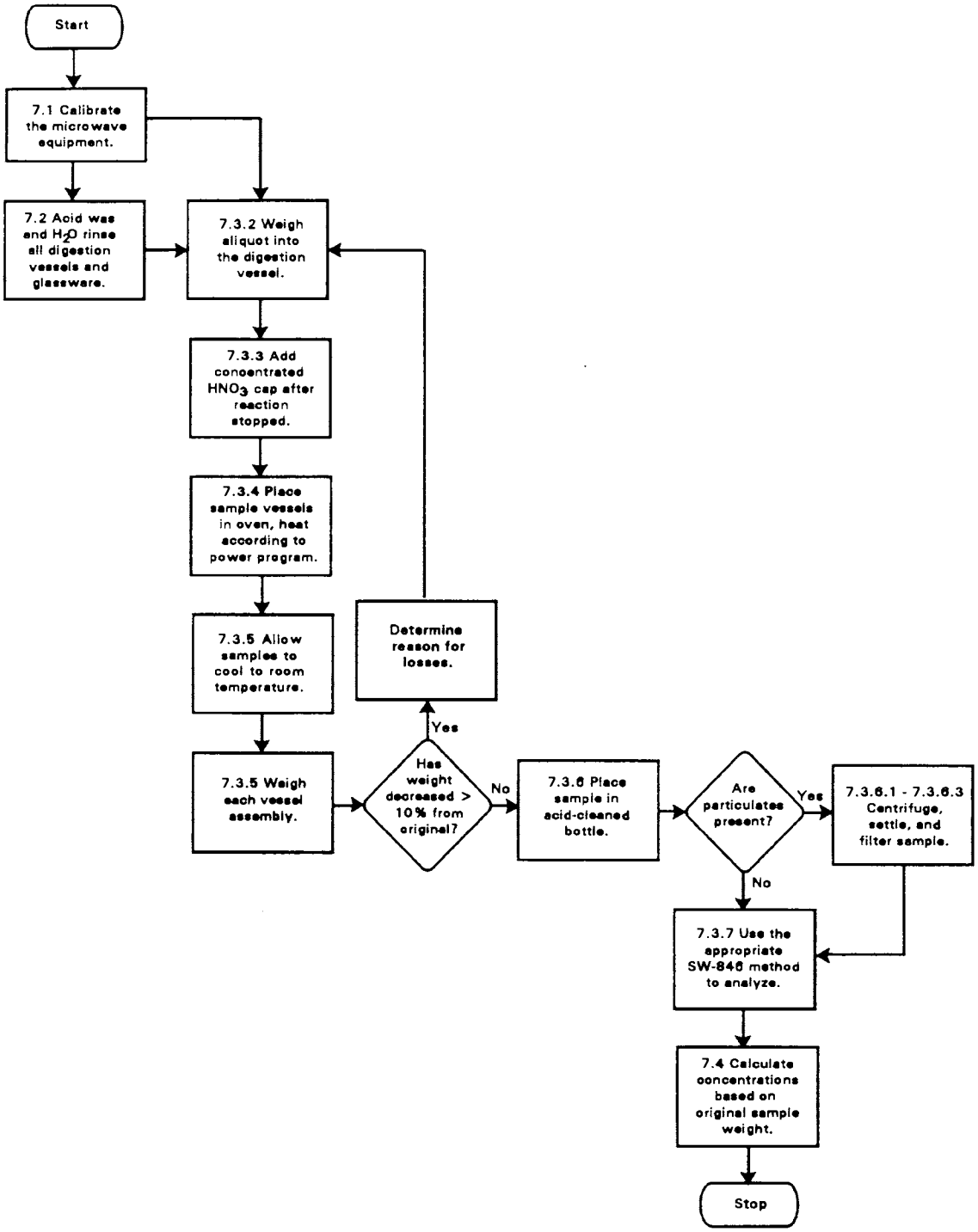
TABLE 3.
RECOVERY AND BIAS DATA FOR SRM 1085 - WEAR METALS IN OIL

Element	Amount Expected (Certified Range)	Amount Found* (95% Conf Interval)	Absolute Bias (µg/g)	Relative Bias (Percent)	Significant (due to more than chance)
Ag	(291)**	234±16	--	--	--
Al	296±4	295±12	-1	0	No
Cr	298±5	293±10	-5	-2	No
Cu	295±10	289±9	-6	-2	No
Fe	300±4	311±14	+11	+4	No
Mg	297±3	270±11	-27	-9	Yes
Mo	292±11	238±11	-54	-18	Yes
Mi	303±7	293±9	-10	-3	No
Pb	(305)**	279±8	--	--	--

All values in mg/Kg

*Results taken from table 4-7, Ref. 2.

**Value not certified, so should not be used in bias detection and estimation.


Start
7.1 Calibrate the microwave equipment.
7.2 Acid was and H_2O rinse all digestion vessels and glassware.
7.3.2 Weigh aliquot into the digestion vessel.
7.3.3 Add concentrated HNO_3 cap after reaction stopped.
7.3.4 Place sample vessels in oven, heat according to power program.
7.3.5 Allow samples to cool to room temperature.
7.3.5 Weigh each vessel assembly.
Has weight decreased > 10% from original?
Yes
Determine reason for losses.
No
7.3.6 Place sample in acid-cleaned bottle.
Are particulates present?
Yes
7.3.6.1 - 7.3.6.3 Centrifuge, settle, and filter sample.
No
7.3.7 Use the appropriate SW-846 method to analyze.
7.4 Calculate concentrations based on original sample weight.
Stop

USEPA METHOD 3051A

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

1.0 SCOPE AND APPLICATION

1.1 This microwave extraction method is designed to mimic extraction using conventional heating with nitric acid (HNO_3), or alternatively, nitric acid and hydrochloric acid (HCl), according to EPA Methods 200.2 and 3050. Since these methods are not intended to accomplish total decomposition of the sample, the extracted analyte concentrations may not reflect the total content in the sample. This method is applicable to the microwave-assisted acid extraction/dissolution‡ of sediments, sludges, soils, and oils for the following elements:

Element		CASRN[a]
Aluminum	(Al)	7429-90-5*
Antimony	(Sb)	7440-36-0*
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3*
Beryllium	(Be)	7440-41-7*
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3*
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6*
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4*
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4*
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2*
Zinc	(Zn)	7440-66-6

[a]Chemical Abstract Service Registry Number

*Indicates elements which typically require the addition of HCl to achieve equivalent results with EPA Method 3050, as noted in reference 3.

‡Note: For matrices such as certain types of oils, this method may or may not provide total sample dissolution. For other matrices, such as soils and sediments, it should be considered an extraction method. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec. 9.0).

1.2 This method is provided as an alternative to EPA Methods 200.2 and 3050. This method provides options for improving the performance for certain analytes, such as antimony, iron, aluminum, and silver by the addition of hydrochloric acid, when necessary. It is intended to provide a rapid multi-element acid extraction or dissolution prior to analysis so that decisions can be made about materials and site cleanup levels, the need for TCLP testing of a waste (see EPA Method 1311, Section 1.2, for further details), and whether a BDAT process is providing acceptable performance. Digests produced by the method are suitable for analysis by flame atomic absorption spectrophotometry (FLAA), graphite furnace atomic absorption spectrophotometry (GFAA), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). However, the addition of HCl may limit the methods of detection, or increase the difficulties of detection with some techniques.

Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is extracted and/or dissolved in 10 mL concentrated nitric acid, or alternatively, 9 mL concentrated nitric acid and 3 mL concentrated hydrochloric acid for 10 minutes using microwave heating with a suitable laboratory microwave unit. The sample and acid(s) are placed in a fluorocarbon polymer (PFA or TFM) or quartz microwave vessel or vessel liner. The vessel is sealed and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate determinative method.

3.0 DEFINITIONS

Please refer to Chapter One and Chapter Three for a listing of applicable definitions.

4.0 INTERFERENCES

4.1 Very reactive samples or volatile materials may create high pressures due to the evolution of gaseous digestion products. This may cause venting of the vessels with potential loss of sample and/or analytes. The complete decomposition of either carbonates, or carbon based samples, may produce enough pressure to vent the vessel if the sample size is greater than 0.25 g (depending on the pressure capability of the vessel). Variations of the method to accommodate very reactive materials are specifically addressed in Section 11.3.3.

4.2 Many types of samples will be dissolved by this method. A few refractory sample matrix compounds, such as quartz, silicates, titanium dioxide, alumina, and other oxides may not be dissolved and in some cases may sequester target analyte elements. These bound elements are considered non-mobile in the environment and are excluded from most aqueous transport mechanisms of pollution.

5.0 SAFETY

5.1 The microwave unit cavity must be corrosion resistant and well ventilated. All electronics must be protected against corrosion for safe operation.

CAUTION: *There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. A listing of these specific suggestions is beyond the scope of this method. The analyst is advised to consult the equipment manual, the equipment manufacturer, and other appropriate literature for proper and safe operation of the microwave equipment and vessels. For further details, see reference 3 and the document of Sec. 13.2.1 for a review of safety in microwave sample preparation.*

5.2 The method requires essentially microwave transparent and reagent resistant materials such as fluorocarbon polymers (examples are PFA or TFM) or quartz to contain acids and samples. For higher pressure capabilities the vessel may be contained within layers of different microwave transparent materials for strength, durability, and safety. The internal volume of the vessel should be at least 45 mL, and the vessel must be capable of withstanding pressures of at least 30 atm (435 psi), and capable of controlled pressure relief. These specifications are to provide an appropriate, safe, and durable reaction vessel of which there are many adequate designs by many suppliers.

CAUTION: *The reagent combination (9 mL nitric acid to 3 mL hydrochloric acid) results in greater pressures than those resulting from the use of only nitric acid. As demonstrated in Figures 1 and 2, pressures of approximately 12 atm have been reached during the heating of the acid mixture alone (no sample in the vessel). Pressures reached during the actual decomposition of a sediment sample (SRM 2704, a matrix with low organic content) have more than doubled when using the 9 mL nitric and 3 mL hydrochloric acid mixture. These higher pressures necessitate the use of vessels having higher pressure capabilities (30 atm or 435 psi). Matrices having large organic content, such as oils, can produce approximately 25 atm of pressure inside the vessel (as described in EPA Method 3052).*

CAUTION: *The outer layers of vessels are frequently not as acid or reagent resistant as the liner material. In order to retain the specified performance and safety requirements, these outer layers must not be chemically degraded or physically damaged. Routine examination of the vessel materials is necessary to ensure their safe use.*

CAUTION: *Another safety concern relates to the use of sealed containers without pressure relief devices. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures, but must be safely contained. Some digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures. Only fluorocarbon (such as PFA or TFM and others) or quartz containers with pressure relief mechanisms or containers with fluorocarbon or quartz liners and pressure relief mechanisms are considered acceptable.*

CAUTION: *Laboratories should not use domestic (kitchen) type microwave ovens for this method because of significant safety issues. When acids such as nitric and hydrochloric are used to effect sample digestion in microwave units in open vessel(s), or sealed vessel(s), there is the potential for any released acid vapors to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a system with isolated and corrosion resistant safety devices prevents this from occurring.*

Users are therefore advised not to use domestic (kitchen) type microwave ovens or sealed containers which are not equipped with controlled pressure relief mechanisms for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details, consult reference 3 and the document listed in Sec. 13.2.1.

6.0 EQUIPMENT AND SUPPLIES

6.1 Microwave apparatus requirements.

6.1.1 The temperature performance requirements necessitate the microwave decomposition system to sense the temperature to within ± 2.5 °C and automatically adjust the microwave field output power within 2 seconds of sensing. Temperature sensors should be accurate to ± 2 °C (including the final reaction temperature of 175 ± 5 °C). Temperature feedback control provides the primary performance mechanism for the method. Due to the variability in sample matrix types and microwave digestion equipment

(i.e., different vessel types and microwave oven designs), temperature feedback control is preferred for reproducible microwave heating. For further details consult reference 3.

Alternatively, for a specific vessel type, specific set of reagent(s), and sample type, a calibration control mechanism can be developed. Through calibration of the microwave power for a specific number and type of vessels, vessel load, and heat loss characteristics of a specific vessel series, the reaction temperature profile described in Sec. 11.3.5 can be reproduced. The calibration settings are specific for the number and type of vessels and microwave system being used, in addition to the specific reagent combination being used. Therefore, no specific calibration settings are provided in this method. These settings may be developed by using temperature monitoring equipment for each specific set of microwave equipment and vessel type. They may be used as previously described in methods such as EPA Methods 3051, 3015, and 3052. In this circumstance, the microwave system provides programmable power, which can be programmed to within ± 12 W of the required power. Typical systems provide a nominal 600 W to 1200 W of power. Calibration control provides backward compatibility with older laboratory microwave systems which may not be equipped for temperature monitoring or feedback control and with lower cost microwave systems for some repetitive analyses. Older vessels with lower pressure capabilities may not be compatible (see refs. 1, 2, and 3 and the documents listed in 13.3.3 and 13.3.5).

6.1.2 The accuracy of the temperature measurement system should be periodically validated at an elevated temperature (see Section 12.2). This can be done using a container of silicon oil (a high temperature oil) and an external, calibrated temperature measurement system. The oil should be adequately stirred to ensure a homogeneous temperature, and both the microwave temperature sensor and the external temperature sensor placed into the oil. After heating the oil to a constant temperature of 180 ± 5 °C, the temperature should be measured using both sensors. If the measured temperatures vary by more than 1 to 2 °C, the microwave temperature measurement system should be calibrated. Consult the microwave manufacturer's instructions about the specific temperature sensor calibration procedure.

6.1.3 A rotating turntable is employed to ensure the homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm. Other types of equipment that are used to assist in achieving uniformity of the microwave field may also be appropriate.

6.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

6.3 Filter paper, qualitative or equivalent.

6.4 Filter funnel, glass, polypropylene, or other appropriate material.

6.5 Analytical balance, of appropriate capacity and resolution meeting data quality objectives.

7.0 REAGENTS

7.1 All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without decreasing the accuracy of the determination. If the purity of a reagent is questionable, the reagent should be analyzed to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

7.1.1 Concentrated nitric acid (HNO_3). The acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

7.1.2 Concentrated hydrochloric acid (HCl). The acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

7.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. For further details, consult the document listed in Sec. 13.3.3.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of SW-846. Refer to that chapter, as updated, for guidance.

8.2 All sample containers must be prewashed with acids and water, and metal-free detergents, if necessary, depending on the history of use of the container (Ref. 3). Plastic and glass containers are both suitable. For further information, see Chapter Three of SW-846.

8.3 Samples must be refrigerated upon receipt and analyzed as soon as possible.

9.0 QUALITY CONTROL

9.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts.

9.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analysis process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

9.3 Spiked samples or standard reference materials should be included with each group of samples processed, or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

9.4 Periodically, the accuracy of the temperature measurement system used to control the microwave equipment should be validated per Section 6.1.2.

9.5 (Not necessary if using temperature feedback control.) Each day that samples are extracted, the microwave-power calibration should be verified by heating 1 kg of ASTM Type II water (at 22 ± 3 °C) in a covered, microwave-transparent vessel for 2 min at the setting for 490 W and measuring the water temperature after heating per Section 10.1.5. If the power calculated (per Section 12) differs from 490 W by more than ± 10 W, the microwave settings should be recalibrated per Section 10.0.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration of Microwave Equipment

NOTE: *If the microwave unit uses temperature feedback control to control the performance specifications of the method, then performing the calibration procedure is not necessary.*

10.1.1 Calibration is the normalization and reproduction of a microwave field strength to permit reagent and energy coupling in a predictable and reproducible manner. It balances reagent heating and heat loss from the vessels and is equipment dependent due to the heat retention and loss characteristics of the specific vessel. Available power is evaluated to permit the microwave field output in watts to be transferred from one microwave system to another.

Use of calibration to control this reaction requires balancing output power, coupled energy, and heat loss to reproduce the temperature heating profile given in Section 11.3.5. The conditions for each acid mixture and each batch containing the same specified number of vessels must be determined individually. Only identical acid mixtures and vessel models and specified numbers of vessels may be used in a given batch.

10.1.2 For cavity type microwave equipment, calibration is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the system. The calibration format required for laboratory microwave systems depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few systems have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (see Section 10.1.4). Otherwise, the analyst must use the multiple point calibration method (see Section 10.1.3). Assistance in calibration and software guidance of calibration are available in reference 3 and the document listed in Sec. 13.3.5.

10.1.3 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured: 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in Section 10.1.5. This data is clustered about the customary working power ranges. Non-linearity has been encountered at the upper end of the calibration. If the system's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (± 10 W), then the entire calibration should be re-evaluated.

10.1.4 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in Section 10.1.5. From this 2-point line, determine the partial power setting that corresponds to the power, in watts, specified in the procedure to reproduce the heating profile specified in Section 11.3.6. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ± 10 W, use the multiple point calibration in Section 10.1.3. This point should also be used to periodically verify the integrity of the calibration.

10.1.5 Equilibrate a large volume of water to room temperature (22 ± 3 °C). One kg of reagent water is weighed (1,000.0 ± 0.1 g) into a fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 22 ± 3 °C measured to ± 0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the system's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation (irradiating with the stir bar in the vessel could cause electrical arcing) and record the maximum temperature

within the first 30 seconds to ± 0.05 °C. Use a new sample for each additional measurement. If the water is reused (after making adjustments for any loss of weight due to heating), both the water and the beaker must have returned to 22 ± 3 °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Equation 1

Where:

P = the apparent power absorbed by the sample in watts (W) (joule/sec)

K = the conversion factor for thermochemical calories sec^{-1} to watts (K= 4.184)

C_p = the heat capacity, thermal capacity, or specific heat [cal/(g °C)] of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes (120 sec) and 1 kg (1000 g) of distilled water [heat capacity at 25 °C is 0.9997 cal/(g °C)] the calibration equation simplifies to:

Equation 2

NOTE: *Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ± 2 V (Reference 3). Electronic components in most microwave units are matched to the system's function and output. When any part of the high voltage circuit, power source, or control components in the system have been serviced or replaced, it will be necessary to recheck the system's calibration. If the power output has changed significantly (± 10 W), then the entire calibration should be re-evaluated.*

11.0 PROCEDURE

11.1 Temperature control of closed vessel microwave instruments provides the main feedback control performance mechanism for the method. Method control requires a temperature sensor in one or more vessels during the entire decomposition. The microwave

decomposition system should sense the temperature to within ± 2.5 °C and permit adjustment of the microwave output power within 2 seconds.

11.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels (fluoropolymer or quartz liners) should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80 °C, but less than boiling) for a minimum of two hours followed by hot (1:1) nitric acid (greater than 80 °C, but less than boiling) for a minimum of two hours. The vessels should then be rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from prior sample digestions in vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific material used and then rinsed with reagent water and dried in a clean environment.

11.3 Sample Digestion

11.3.1 Weigh a well-mixed sample to the nearest 0.001 g into an appropriate vessel equipped with a controlled pressure relief mechanism. For soils, sediments, and sludges, use no more than 0.500 g. For oil or oil contaminated soils, initially use no more than 0.250 g. When large samples of oil are necessary, use of EPA Method 3052, which has sample scale-up options, is recommended. If the sample can not be well mixed and homogenized on an as received basis, then air or oven drying at 60°C or less, crushing, sieving, grinding, and mixing should be performed as necessary to homogenize the sample until the subsampling variance is less than the data quality objectives of the analysis. While proper sample preparation generally produces great reduction in analytical variability, be aware that in certain unusual circumstances there could be loss of volatile metals (e.g., Hg, organometallics) or irreversible chemical changes (e.g., precipitation of insoluble species, change in valence state). See Chapter Three for more details.

11.3.2 Add 10 ± 0.1 mL concentrated nitric acid or, alternatively, 9 ± 0.1 mL concentrated nitric acid and 3 ± 0.1 mL concentrated hydrochloric acid to the vessel in a fume hood (or fume exhausted enclosure). The addition of concentrated hydrochloric acid to the nitric acid is appropriate for the stabilization of certain analytes, such as Ag, Ba, and Sb and high concentrations of Fe and Al in solution. Improvements and optimal recoveries of antimony, iron, and silver from a variety of matrices upon addition of HCl are demonstrated in Section 17.0, in Figures 3 through 7. The addition of hydrochloric acid may, however, limit the detection techniques or increase the difficulties of analysis for some detection systems.

CAUTION: *The addition of hydrochloric acid must be in the form of concentrated hydrochloric acid and not from a premixed combination of acids as a buildup of chlorine gas, as well as other gases, will result from a premixed acid solution. These gases may be violently released upon heating. This is avoided by adding the acid in the described manner.*

CAUTION: *Toxic nitrogen oxide(s) and chlorine fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a properly operating fume ventilation system.*

CAUTION: *The analyst should wear protective gloves and face protection.*

CAUTION: *The use of microwave equipment with temperature feedback control is required to control any unfamiliar reactions that may occur during the leaching of samples of unknown composition. The leaching of these samples may require additional vessel requirements such as increased pressure capabilities.*

11.3.3 The analyst should be aware of the potential for a vigorous reaction, especially with samples containing volatile or easily oxidized organic species. When digesting a matrix of this type, initially use no more than 0.100 g of sample. If a vigorous reaction occurs upon the addition of reagent(s), allow the sample to predigest in the uncapped digestion vessel until the reaction ceases. Heat may be added in this step for safety considerations (for example, the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure. However, if no appreciable reaction occurs, a sample mass of up to 0.250 g for oils, or 0.500 g for solids, may be used.

11.3.4 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and, when applicable, connect appropriate temperature and pressure sensors to vessels according to manufacturer's specifications.

11.3.5 This method is a performance based method, designed to achieve or approach consistent leaching of the sample through achieving specific reaction conditions. The temperature of each sample should rise to 175 ± 5 °C in approximately 5.5 ± 0.25 minutes and remain at 175 ± 5 °C for 4.5 minutes, or for the remainder of the ten minute digestion period (see Refs. 2, 3, and 4 and the document listed in 13.3.4). The time versus temperature and pressure profile is given for a standard sediment sample in Figure 2. When using temperature feedback control, the number of samples that may be simultaneously digested may vary, from one sample up to the maximum number of vessels that can be heated by the magnetron of the microwave unit according to the heating profile specified previously in this section. (The number will depend on the power of the unit, the number of vessels, and the heat loss from the vessels (Ref. 3)).

The pressure should peak between 5 and 10 minutes for most samples (see Refs. 1 and 2 and the document listed in 13.3.4). If the pressure exceeds the pressure limits of the vessel, the pressure should be safely and controllably reduced by the pressure relief mechanism of the vessel.

> **11.3.5.1** Calibration control is applicable in reproducing this method provided the power in watts versus time parameters are determined to reproduce the specifications listed in 11.3.5. The calibration settings will be specific to the quantity of reagents, the number of vessels, and the heat loss characteristics of the vessels (see Ref. 3 and the document listed in Sec. 13.3.3). If calibration control is being used, any vessels containing acids for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with the same acid mixture to achieve the full complement of vessels. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbing mass in the cavity. Irradiate each group of vessels using the predetermined calibration settings. (Different vessel types should not be mixed).

11.3.6 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave system. Cooling of the vessels may be accelerated by internal or external cooling devices. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained their seal throughout the digestion. Due to the wide variability of vessel designs, a single procedure is not appropriate. For vessels that are sealed as discrete separate entities, the vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised. For vessels with burst disks, a careful visual inspection of the disk, in addition to weighing, may identify compromised vessels. For vessels with resealing pressure relief mechanisms, an auditory or a physical sign that can indicate whether a vessel has vented is appropriate.

11.3.7 Complete the preparation of the sample by carefully uncapping and venting each vessel in a chemical fume hood (or fume exhausted enclosure). Vent the vessels using the procedure recommended by the vessel manufacturer. Quantitatively transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged (11.3.7.1), allowed to settle (11.3.7.2), or filtered (11.3.7.3).

11.3.7.1 Centrifugation: Centrifugation at 2,000 - 3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

11.3.7.2 Settling: If undissolved material, such as SiO_2, TiO_2, or other refractory oxides, remains, allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

11.3.7.3 Filtering: If necessary, the filtering apparatus must be thoroughly cleaned and pre-rinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

11.3.8 The removal or reduction of the quantity of the nitric and hydrochloric acids prior to analysis may be desirable. The chemistry and volatility of the analytes of interest should be considered and evaluated when using this alternative (Reference 3). Evaporation to near dryness in a controlled environment with controlled purge gas and neutralizing and collection of exhaust interactions is an alternative where appropriate. This manipulation may be performed in the microwave system, if the system is capable of this function, or external to the microwave system in more common apparatus(s). This option must be tested and validated to determine analyte retention and loss and should be accompanied by equipment validation possibly using the standard addition method and standard reference materials. This alternative may be used to alter either the acid concentration and/or acid composition prior to analysis. (For further information, see reference 3 and Method 3052).

NOTE: *The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable. Waste minimization techniques should be used to capture reagent fumes. This procedure should be tested and validated in the apparatus and on standards before using on unknown samples.*

11.3.9 Transfer or decant the sample into volumetric ware and dilute the digest to a known volume. The digest is now ready for analysis for elements of interest using appropriate elemental analysis techniques and/or SW-846 methods.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

12.2 Prior to use of the method, verify that the temperature sensing equipment is properly reading temperature. A procedure for verification is given in Section 6.1.2. This will establish the accuracy and precision of the temperature sensing equipment, which should be carried throughout the statistical treatment of the quality assurance data.

12.3 In calibrating the microwave unit (Section 10.0), the power absorbed (for each power setting) by 1 kg of reagent water exposed to 120 seconds of microwave energy is determined by the expression:

Power (in watts) = $(T_1 - T_2)$ (34.86)

where: T_1 = Initial temperature of water (between 21 and 25 °C to nearest 0.1 °C)

T_2 = Final temperature of water (to nearest 0.1 °C)

12.4 Plot the power settings against the absorbed power (calculated in Section 12.3) to obtain a calibration relationship. Alternatively, use a microwave calibration program to analyze the calibration data (see Ref. 3 and the document listed in Sec. 13.3.5). Interpolate the data to obtain the instrument settings needed to provide the wattage levels specified in Section 12.3.

12.5 Calculate the sample dry-weight fraction as follows:

Dry-Wt fraction =

where: W_1 = Wt for sample + vessel, before drying, g

W_2 = Wt for sample + vessel, after drying, g

W_3 = Wt for empty, dry vessel, g

12.6 Convert the extract concentration obtained from the instrument in mg/L to mg/kg dry-weight of sample by:

Sample concentration =

where: C = Concentration in extract (mg/L)

D = Dilution factor

S = Solid dry-weight fraction for sample, g/g

V = Volume of extract, mL x 0.001

W = Weight of undried sample extracted, g x 0.001

13.0 METHOD PERFORMANCE

13.1 The fundamental chemical basis of Method 3051 with and without HCl has been compared with Method 3050 in several sources (see 13.3.4 and 13.3.5). Several papers have evaluated the leachability of NIST SRMs with this method (Ref. 1 and Sec. 13.3.5). Evaluations and optimizations of this method are being published (Ref. 5 and 6) as well as additional

leaches performed on more matrices, which will be addressed in future literature papers. Method 3051 has been determined to be appropriate for enhancing recoveries of certain analytes. This data is contained in Section 17 of this method. Matrices tested include SRM 2710 (Montana Soil - Highly Elevated Concentrations), SRM 2704 (Buffalo River Sediment), and SRM 1084a (Wear Metals in Oil). Analytes demonstrating better recoveries upon addition of HCl include antimony, iron, and silver.

13.2 The following documents may provide additional guidance and insight on this method and technique:

13.2.1 Kingston, H. M. and L. B. Jassie, "Safety Guidelines for Microwave Systems in the Analytical Laboratory". In Introduction to Microwave Acid Decomposition: Theory and Practice; Kingston, H.M. and Jassie, L.B., eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988.

13.2.2 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water" ; ASTM, Philadelphia, PA, 1985, D1193-77.

13.3.3 Introduction to Microwave Sample Preparation: Theory and Practice, Kingston, H.M. and Jassie, L.B., Eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988.

13.3.4 Kingston, H.M., Walter, P.J., "Comparison of Microwave Versus Conventional Dissolution for Environmental Applications", Spectroscopy, Vol. 7 No. 9, 20-27, 1992.

13.3.5 Walter, P. J. Special Publication IR4718: *Microwave Calibration Program*, 2.0 ed.; National Institutes of Standards and Technology: Gaithersburg, MD, 1991.

13.3.6 Kingston, H.M., Walter, P.J., Chalk, S.J., Lorentzen, E.M., Link, D.D., "Environmental Microwave Sample Preparation: Fundamentals, Methods, and Applications". In Microwave Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications; ACS Professional Reference Book Series; American Chemical Society: Washington, DC 1997.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult Less is Better: Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer

discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036, (202) 872-4477.

16.0 REFERENCES

1. Kingston, H.M. EPA IAG #DWI-393254-01-0 January 1-March 31, 1988, quarterly report.

2. Binstock, D.A., Yeager, W.M., Grohse, P.M. and Gaskill, A. Validation of a Method for Determining Elements in Solid Waste by Microwave Digestion, Research Triangle Institute Technical Report Draft, RTI Project Number 321U-3579-24, November, 1989, prepared for the Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC 20460.

3. Kingston, H.M., Haswell, S, Microwave Enhanced Chemistry: Fundamentals, Sample Preparation, and Applications; ACS Professional Reference Book Series; American Chemical Society: Washington, DC 1997.

4. Binstock, D.A., Grohse, P.M., Gaskill, A., Sellers, C., Kingston, H.M., Jassie, L.B., "Development and Validation of a Method for Determining Elements in Solid Waste using Microwave Digestion", J. Assoc. Off. Anal. Chem., Vol. 74, 360 - 366 , 1991.

5. Kingston, H.M., Walter, P.J., Lorentzen, E.M.L., Lusnak, G.P. "The Performance of Leaching Studies on Soil SRM's 2710 and 2711"; Final Report to the National Institute of Standards and Technology, Duquesne University: Pittsburgh, PA, April 5, 1994.

6. Link, D.D., Kingston, H.M., Walter, P.J., "Development and Validation of the New EPA Microwave-assisted Leach Method 3051A".

7. Link, DD., Kingston, H.M., Walter, P.J.; *Development and Validation of the EPA Microwave-assisted Methods 3015A and 3051A:* Validation Studies for Updated Microwave Leach Methods, Proceedings for the Waste Testing and Quality Assurance Symposium; July 1997.

8. Kingston, H.M., Walter, P.J., "Comparison of Microwave verses Conventional Dissolution for Environmental Applications", Spectroscopy, Vol. 7 No. 9, 20-27, 1992.

9. Walter, P.J. Special Publication IR7718: Microwave Calibration Program, 2.0 ed.; National Institute of Standards and Technology: Gaithersburg, MD, 1991.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 3, Figures 1 through 7, and a flow diagram of method procedure.

TABLE 1

COMPARISON OF ANALYTE RECOVERIES FROM SRM 2704 (BUFFALO RIVER SEDIMENT) USING BOTH DIGEST OPTIONS OF METHOD 3051 (Refs. 5, 6)

Element	10 mL HNO_3	9 mL HNO_3 +	Total Analyte Concentration

Results reported in μg/g analyte (mean ± 95% confidence limit).

Total concentrations are taken from NIST SRM Certificate of Analysis.

TABLE 2

COMPARISON OF ANALYTE RECOVERIES FROM SRM 4355 (PERUVIAN SOIL)

USING BOTH DIGEST OPTIONS OF METHOD 3051 (Ref. 6).

Element	10 mL HNO_3	9 mL HNO_3 +	Total Analyte Concentration

Results reported in μg/g analyte (mean ± 95% confidence limit).

Total concentrations are taken from NIST SRM Certificate of Analysis.

Values in parenthesis are reference concentrations.

TABLE 3

COMPARISON OF ANALYTE RECOVERIES FROM SRM 1084A (WEAR METALS IN OIL)
USING BOTH DIGEST OPTIONS OF METHOD 3051 (Ref. 6)

Element	10 mL HNO_3	9 mL HNO_3 +	Total Analyte Concentration

Results reported in μg/g analyte (mean ± 95% confidence limit).

Total concentrations are taken from NIST SRM Certificate of Analysis.

FIGURE 1

TEMPERATURE AND PRESSURE PROFILES FOR THE HEATING OF DIFFERENT RATIOS OF NITRIC ACID TO HYDROCHLORIC ACID USING METHOD 3051

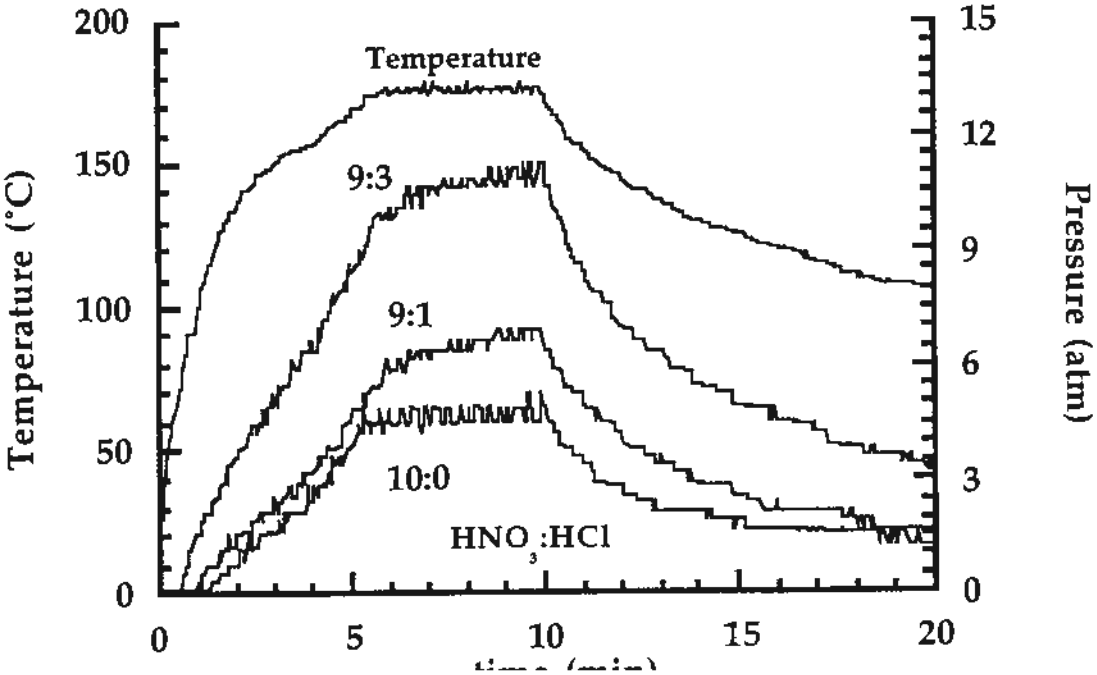


FIGURE 2

TEMPERATURE AND PRESSURE PROFILE FOR THE EXTRACTION AND DISSOLUTION OF NIST SRM 2704 (BUFFALO RIVER SEDIMENT) USING DIFFERENT RATIOS OF NITRIC ACID TO HYDROCHLORIC ACID

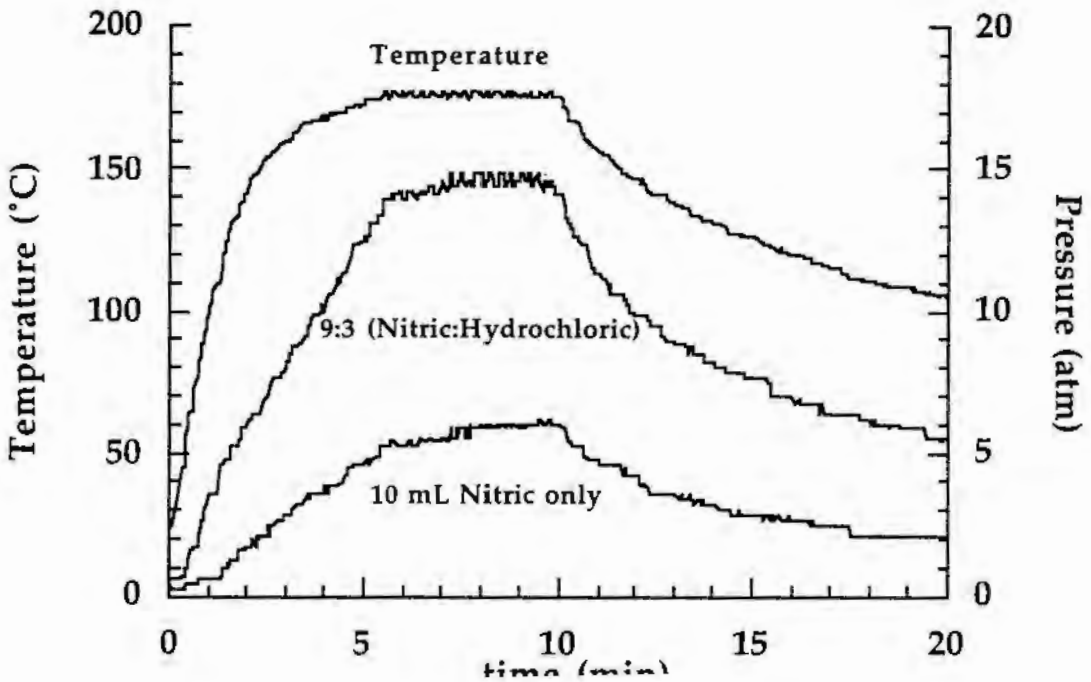


FIGURE 3

PERCENT RECOVERY OF ANTIMONY FROM NIST SRM 2710 (MONTANA SOIL) VERSUS VARIOUS COMBINATIONS OF NITRIC AND HYDROCHLORIC ACIDS (N=6) (Refs. 6, 7)

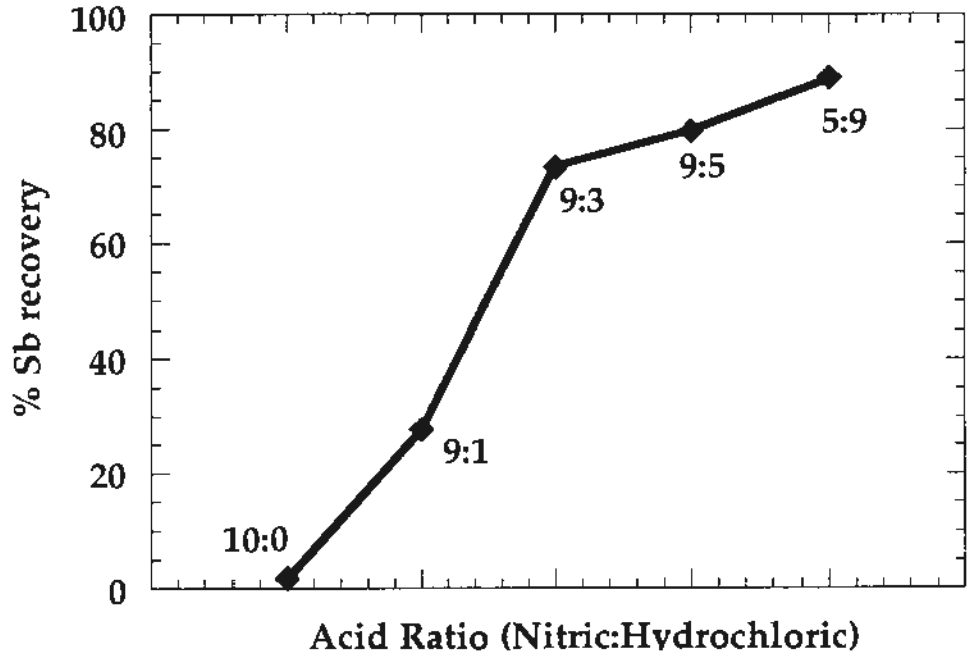


FIGURE 4

PERCENT RECOVERY OF ANTIMONY FROM NIST SRM 2704 (BUFFALO RIVER SEDIMENT) VERSUS VARIOUS COMBINATIONS OF NITRIC AND HYDROCHLORIC ACIDS (N=6) (Refs. 6, 7).

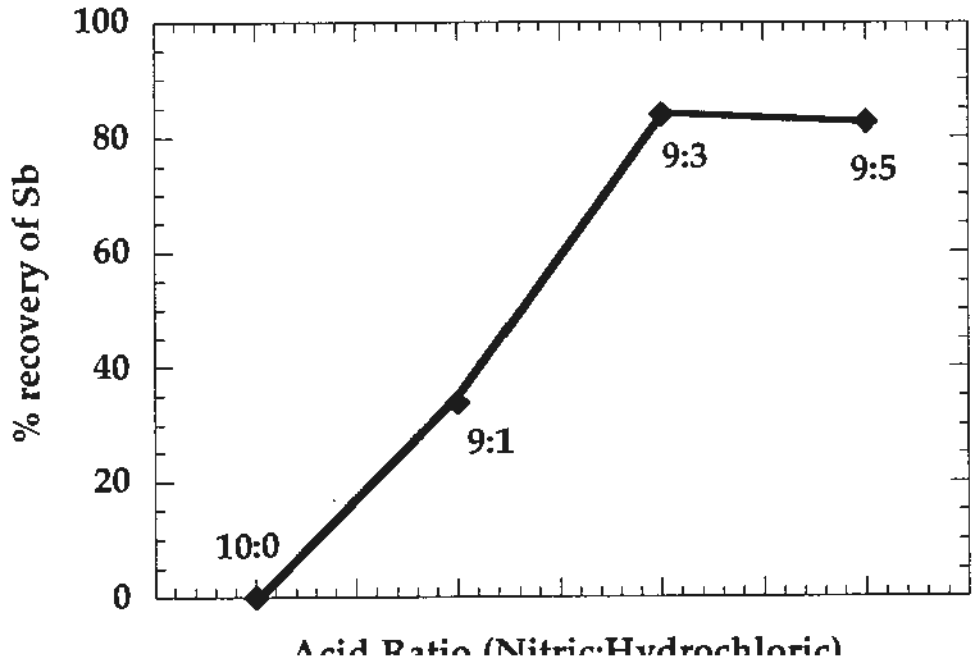


FIGURE 5

PERCENT RECOVERY OF IRON FROM NIST SRM 2704 (BUFFALO RIVER SEDIMENT) VERSUS VARIOUS COMBINATIONS OF NITRIC AND HYDROCHLORIC ACIDS (N=6) (Refs. 6, 7).

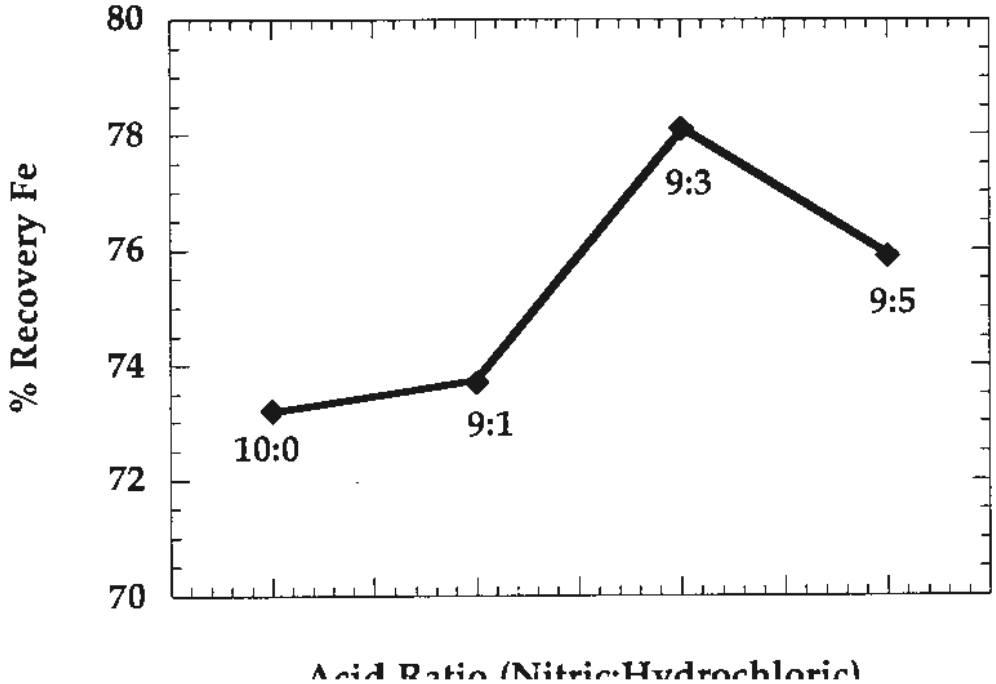


FIGURE 6

PERCENT RECOVERY OF SILVER FROM NIST SRM 2710 (MONTANA SOIL) VERSUS VARIOUS COMBINATIONS OF NITRIC AND HYDROCHLORIC ACIDS (N=6) (Refs. 6, 7)

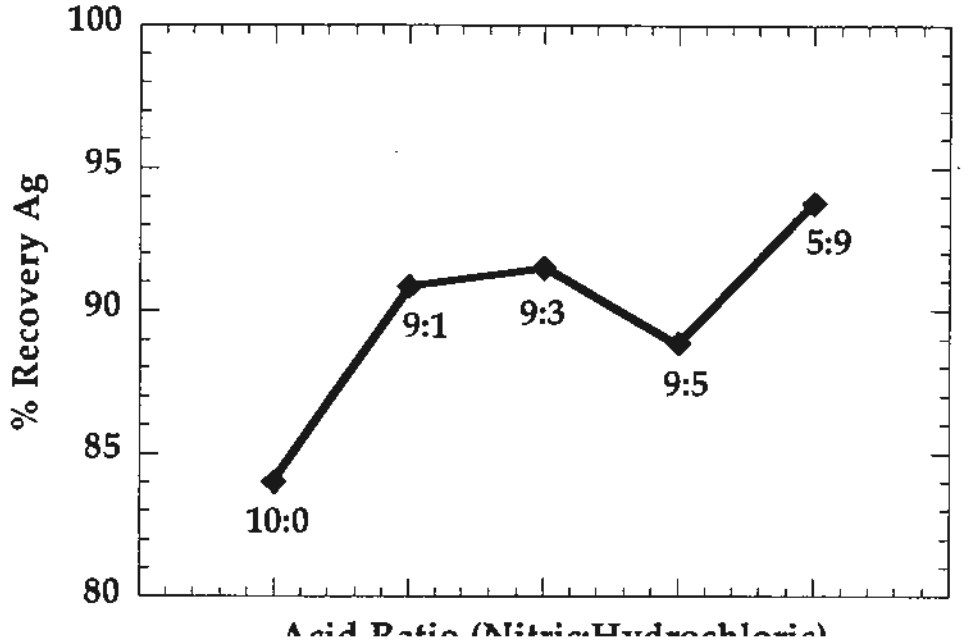
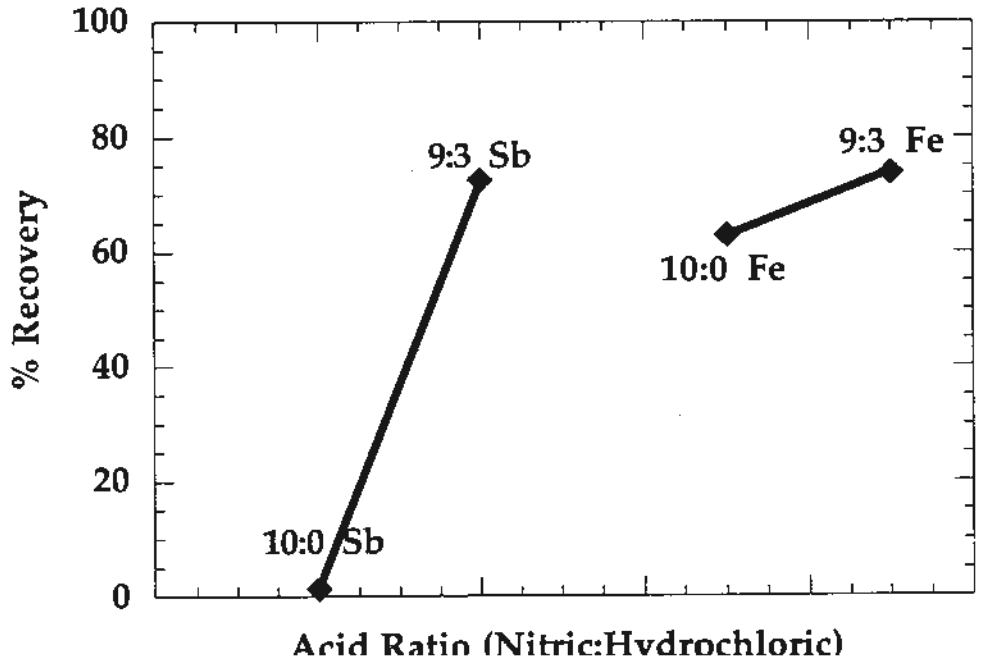


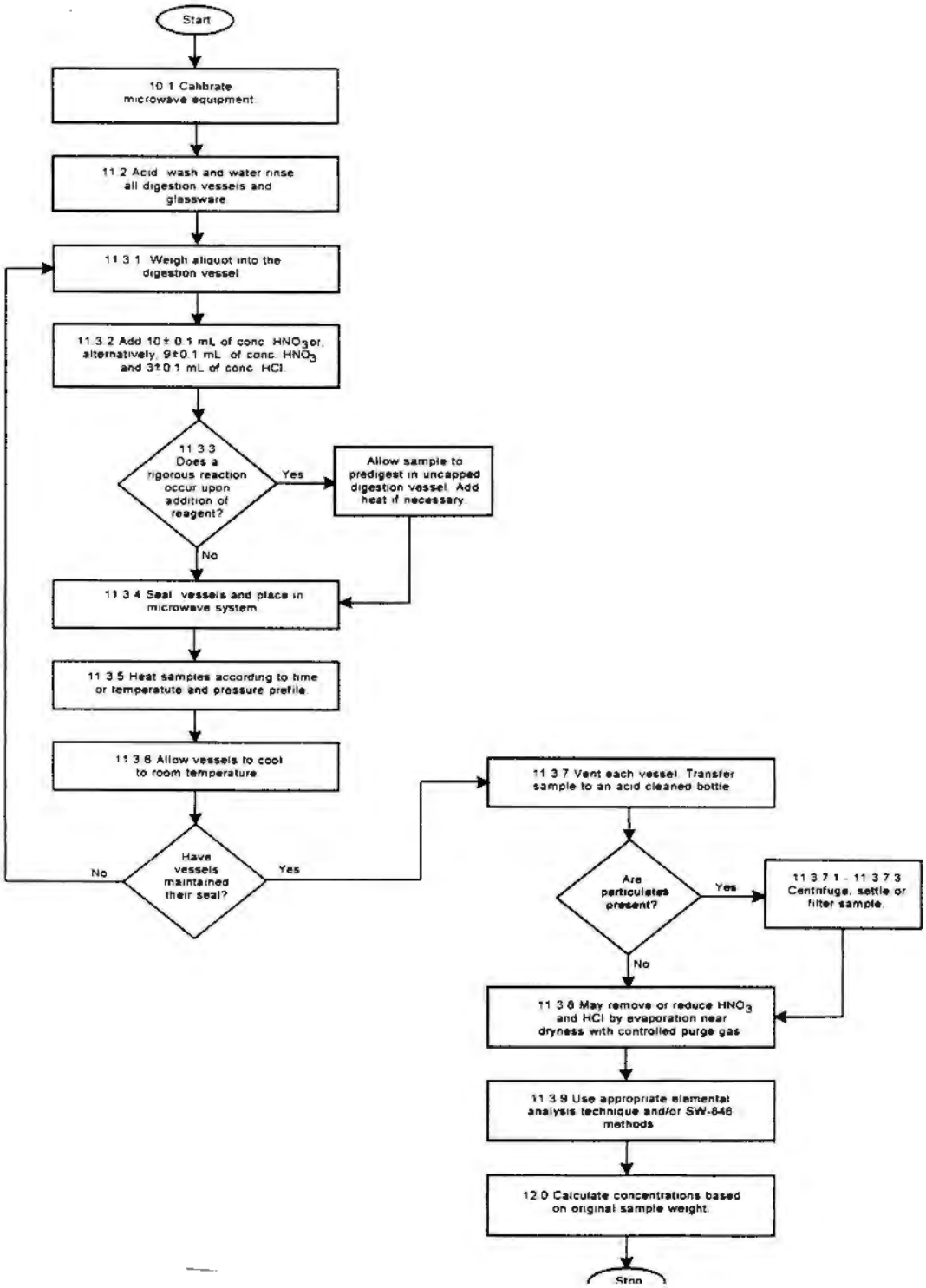
FIGURE 7

PERCENT RECOVERY OF ANTIMONY AND IRON, RESPECTIVELY, FROM SRM 4355 (PERUVIAN SOIL) USING BOTH DIGEST OPTIONS (10 ML HNO_3 AND 9 ML HNO_3 + 3 ML HCL) OF METHOD 3051 (N=6) (Refs. 6, 7)



METHOD 3051A

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS



METHOD 3052

MICROWAVE ASSISTED ACID DIGESTION OF SILICEOUS AND ORGANICALLY BASED MATRICES

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of siliceous matrices, and organic matrices and other complex matrices. If a total decomposition analysis (relative to the target analyte list) is required, the following matrices can be digested: ashes, biological tissues, oils, oil contaminated soils, sediments, sludges, and soils. This method is applicable for the following elements:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Mercury	Silver	Zinc
Beryllium				

Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Sec. 8.0).

> Note: This technique is not appropriate for regulatory applications that require the use of leachate preparations (i.e., Method 3050, Method 3051, Method 1311, Method 1312, Method 1310, Method 1320, Method 1330, Method 3031, Method 3040). This method is appropriate for those applications requiring a total decomposition for research purposes (i.e., geological studies, mass balances, analysis of Standard Reference Materials) or in response to a regulation that requires total sample decomposition.

1.2 This method is provided as a rapid multi-element, microwave assisted acid digestion prior to analysis protocol so that decisions can be made about the site or material. Digests and alternative procedures produced by the method are suitable for analysis by flame atomic absorption spectrometry (FLAA), cold vapor atomic absorption spectrometry (CVAA), graphite furnace atomic absorption spectrometry (GFAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and other analytical elemental analysis techniques where applicable. Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to this manual's "Disclaimer" when conducting analyses using Method 3052.

1.3 The goal of this method is total sample decomposition and with judicious choice of acid combinations this is achievable for most matrices (see Sec. 3.2). Selection of reagents which give the highest recoveries for the target analytes is considered the optimum method condition.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 9 mL of concentrated nitric acid and usually 3 mL hydrofluoric acid for 15 minutes using microwave heating with a suitable laboratory microwave system. The method has several additional alternative acid and reagent combinations including hydrochloric acid and hydrogen peroxide. The method has provisions for scaling up the sample size to a maximum of 1.0 g. The sample and acid are placed in suitably inert polymeric microwave vessels. The vessel is sealed and heated in the microwave system. The temperature profile is specified to permit specific reactions and incorporates reaching 180 ± 5 ºC in approximately less than 5.5 minutes and remaining at 180 ± 5 ºC for 9.5 minutes for the completion of specific reactions (Ref. 1, 2, 3, 4). After cooling, the vessel contents may be filtered, centrifuged, or allowed to settle and then decanted, diluted to volume, and analyzed by the appropriate SW-846 method.

3.0 INTERFERENCES

3.1 Gaseous digestion reaction products, very reactive, or volatile materials that may create high pressures when heated and may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g. Variations of the method due to very reactive materials are specifically addressed in sections 7.3.4 and 7.3.6.1.

3.2 Most samples will be totally dissolved by this method with judicious choice of the acid combinations. A few refractory sample matrix compounds, such as TiO_2, alumina, and other oxides may not be totally dissolved and in some cases may sequester target analyte elements.

3.3 The use of several digestion reagents that are necessary to either completely decompose the matrix or to stabilize specific elements may limit the use of specific analytical instrumentation methods. Hydrochloric acid is known to interfere with some instrumental analysis methods such as flame atomic absorption (FLAA) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The presence of hydrochloric acid may be problematic for graphite furnace atomic absorption (GFAA) and inductively coupled plasma mass spectrometry (ICP-MS). Hydrofluoric acid, which is capable of dissolving silicates, may require the removal of excess hydrofluoric acid or the use of specialized non-glass components during instrumental analysis. Method 3052 enables the analyst to select other decomposition reagents that may also cause problems with instrumental analyses necessitating matrix matching of standards to account for viscosity and chemical differences.

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1 The temperature performance requirements necessitate the microwave decomposition system sense the temperature to within ± 2.5°C and automatically adjust the microwave field output power within 2 seconds of sensing. Temperature sensors should be accurate to ± 2°C (including the final reaction temperature of 180°C). Temperature feedback control provides the primary control performance mechanism for the method. Due to the flexibility in the reagents used to achieve total analysis, tempertuare feedback control is necessary for reproducible microwave heating.

Alternatively, for a specific set of reagent(s) combination(s), quantity, and specific vessel type, a calibration control mechanism can be developed similar to previous microwave methods (see Method 3051). Through calibration of the microwave power, vessel load and heat loss, the reaction temperature profile described in Section 7.3.6 can be reproduced. The calibration settings are specific for the number and type of vessel used and for the microwave system in addition to the variation in reagent combinations. Therefore no specific calibration settings are provided in this method. These settings may be developed by using temperature monitoring equipment for each specific set of equipment and reagent combination. They may only be used if not altered as previously described in other methods such as 3051 and 3015. In this circumstance, the microwave system provides programmable power which can be programmed to within ± 12 W of the required power. Typical systems provide a nominal 600 W to 1200 W of power (Ref. 1, 2, 5). Calibration control provides backward compatibility with older laboratory microwave systems without temperature monitoring or feedback control and with lower cost microwave systems for some repetitive analyses. Older lower pressure vessels may not be compatible.

4.1.2 The temperature measurement system should be periodically calibrated at an elevated temperature. Pour silicon oil (a high temperature oil into a beaker and adequately stirred to ensure a homogeneous temperature. Place the microwave temperature sensor and a calibrated external temperature measurement sensor into the beaker. Heat the beaker to a constant temperature of 180 ± 5°C. Measure the temperature with both sensors. If the measured temperatures vary by more than 1 - 2°C, the microwave temperature measurement system needs to be calibrated. Consult the microwave manufacturer's instructions about the specific temperature sensor calibration procedure.

> CAUTION: The use of microwave equipment with temperature feedback control is required to control the unfamiliar reactions of unique or untested reagent combinations of unknown samples. These tests may require additional vessel requirements such as increased pressure capabilities.

4.1.3 The microwave unit cavity is corrosion resistant and well ventilated. All electronics are protected against corrosion for safe operation.

> CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. A listing of these specific suggestions is beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer, and literature for proper and safe operation of the microwave equipment and vessels.

4.1.4 The method requires essentially microwave transparent and reagent resistant suitably inert polymeric materials (examples are PFA or TFM suitably inert polymeric polymers) to contain acids and samples. For higher pressure capabilities the vessel may be contained within layers of different microwave transparent materials for strength, durability, and safety. The vessels internal volume should be at least 45 mL, capable of withstanding pressures of at least 30 atm (30 bar or 435 psi), and capable of controlled pressure relief. These specifications are to provide an appropriate, safe, and durable reaction vessel of which there are many adequate designs by many suppliers.

CAUTION: The outer layers of vessels are frequently not as acid or reagent resistant as the liner material and must not be chemically degraded or physically damaged to retain the performance and safety required. Routine examination of the vessel materials may be required to ensure their safe use.

CAUTION: The second safety concern relates to the use of sealed containers without pressure relief devices. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures, but must be safely contained. However, many digestion vessels constructed from certain suitably inert polymerics may crack, burst, or explode in the unit under certain pressures. Only suitably inert polymeric (such as PFA or TFM and others) containers with pressure relief mechanisms or containers with suitably inert polymeric liners and pressure relief mechanisms are considered acceptable.

Users are therefore advised not to use domestic (kitchen) type microwave ovens or to use inappropriate sealed containers without pressure relief for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details, consult Reference 3 and 6.

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within most systems (Ref. 1). The speed of the turntable should be a minimum of 3 rpm.

CAUTION: Laboratories should not use domestic (kitchen) type microwave ovens for this method. There are several significant safety issues. First, when an acid such as nitric is used to effect sample digestion in microwave units in open vessel(s), or sealed vessels equipment, there is the potential for the acid gas vapor released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a system with isolated and corrosion resistant safety devices prevents this from occurring.

4.2 Volumetric ware, volumetric flasks, and graduated cylinders, 50 and 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Filter funnel, polypropylene, polyethylene or equivalent.

4.5 Analytical balance, of appropriate capacity, with a ± 0.0001 g or appropriate precision for the weighing of the sample. Optionally, the vessel with sample and reagents may be weighed, with an appropriate precision balance, before and after microwave processing to evaluate the seal integrity in some vessel types.

5.0 REAGENTS

5.1 All reagents should be of appropriate purity or high purity (acids for example, should be sub-boiling distilled where possible) to minimize the blank levels due to elemental contamination. All references to water in the method refer to reagent water (Ref. 7). Other reagent grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Sec. 3.1.3 of this manual, for further information.

6.3 Refer to Chapter Three for the appropriate holding times and storage conditions.

7.0 PROCEDURE

7.1 Temperature control of closed vessel microwave instruments provides the main feedback control performance mechanism for the method. Control requires a temperature sensor in one or more vessels during the entire decomposition. The microwave decomposition system should sense the temperature to within ± 2.5 ^{o}C and permit adjustment of the microwave output power within 2 seconds.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels (fluoropolymer liners only) should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80^{o}C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80^{o}C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware (not used with HF) and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh a well-mixed sample to the nearest 0.001 g into an appropriate vessel equipped with a pressure relief mechanism. For soils, ash, sediments, sludges, and siliceous wastes, initially use no more than 0.5 g. For oil or oil contaminated soils, initially use no more than 0.25 g.

7.3.2 Add 9 ± 0.1 mL concentrated nitric acid and 3 ± 0.1 mL concentrated hydrofluoric acid to the vessel in a fume hood. If the approximate silicon dioxide content of the sample is known, the quantity of hydrofluoric acid may be varied from 0 to 5 mL for stoichiometric reasons. Samples with higher concentrations of silicon dioxide (> 70%) may require higher concentrations of hydrofluoric acid (>3 mL HF). Alternatively samples with lower concentrations of silicon dioxide (< 10% to 0%) may require much less hydrofluoric acid (0.5 mL to 0 mL). Examples are presented in Table 1, 2, 3, and 6. Acid digestion reagent combinations used in the analysis of several matrices, listed in Table 7, provide guidance for the development of new matrix decomposition procedures.

7.3.3 The addition of other reagents with the original acids prior to digestion may permit more complete oxidation of organic sample constituents, address specific decomposition chemistry requirements, or address specific elemental stability and solubility problems.

The addition of 2 ± 2 mL concentrated hydrochloric acid to the nitric and hydrofluoric acids is appropriate for the stabilization of Ag, Ba, and Sb and high concentrations of Fe and Al in solution. The amount of HCl needed will vary depending on the matrix and the concentration of the analytes. The addition of hydrochloric acid may; however, limit the techniques or increase the difficulties of analysis. Examples are presented in Table 4.

The addition of hydrogen peroxide (30%) in small or catalytic quantities (such as 0.1 to 2 mL) may aid in the complete oxidation of organic matter.

The addition of water (double deionized) may (0 to 5 mL) improve the solubility of minerals and prevent temperature spikes due to exothermic reactions.

NOTE: Supporting documentation for the chemistry of this method has been prepared in chapters 2 and 3 of reference 3. It provides additional guidance and documentation of appropriate reagent, matrix and analyte combinations that can be employed in this method.

CAUTION: Only one acid mixture or quantity may be used in a single batch in the microwave to insure consistent reaction conditions between all vessels and monitored conditions. This limitation is due to the current practice of monitoring a representative vessel and applying a uniform microwave field to reproduce these reaction conditions within a group of vessels being simultaneously heated.

CAUTION: Toxic nitrogen oxide(s), hydrogen fluoride, and toxic chlorine (from the addition of hydrochloric acid) fumes are usually produced during digestion. Therefore, all steps involving open or the opening of microwave vessels must be performed in a properly operating fume ventilation system.

CAUTION: The analyst should wear protective gloves and face protection and must not at any time permit a solution containing hydrofluoric acid to come in contact with skin or lungs.

CAUTION: The addition of hydrochloric acid must be from concentrated hydrochloric acid and not from a premixed combination of acids as a buildup of toxic chlorine and possibly other gases will result from a premixed acid solution. This will over pressurize the vessel due to the release of these gases from solution upon heating. The gas effect is greatly lessened by following this suggestion.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

CAUTION: The addition of hydrogen peroxide should only be done when the reactive components of the sample are known. Hydrogen peroxide may react rapidly and violently on easily oxidizable materials and should not be added if the sample may contain large quantities of easily oxidizable organic constituents.

7.3.4 The analyst should be aware of the potential for a vigorous reaction. If a vigorous reaction occurs upon the initial addition of reagent or the sample is suspected of containing easily oxidizable materials, allow the sample to predigest in the uncapped digestion vessel. Heat may be added in this step for safety considerations (for example the rapid release of carbon dioxide from carbonates, easily oxidized organic matter, etc.). Once the initial reaction has ceased, the sample may continue through the digestion procedure.

7.3.5 Seal the vessel according to the manufacturer's directions. Properly place the vessel in the microwave system according to the manufacturer's recommended specifications and connect appropriate temperature and pressure sensors to vessels according to manufacturer's specifications.

7.3.6 This method is a performance based method, designed to achieve or approach total decomposition of the sample through achieving specific reaction conditions. The temperature of each sample should rise to 180 ± 5 ºC in approximately 5.5 minutes and remain at 180 ± 5 ºC for 9.5 minutes. The temperature-time and pressure-time profile are given for a standard soil sample in Figure 1. The number of samples simultaneously digested is dependent on the analyst. The number may range from 1 to the maximum number of vessels that the microwave units magnetron can heat according to the manufacturer's or literature specifications (the number will depend on the power of the unit, the quantity and combination of reagents, and the heat loss from the vessels).

The pressure should peak between 5 and 15 minutes for most samples (Ref. 2, 3, 5). If the pressure exceeds the pressure limits of the vessel, the pressure will be reduced by the relief mechanism of the vessel.

The total decomposition of some components of a matrix may require or the reaction kinetics are dramatically improved with higher reaction temperatures. If microwave digestion systems and/or vessels are capable of achieving higher temperatures and pressures, the minimum digestion time of 9.5 minutes at a temperature of at least 180 ± 5°C is an appropriate

alternative. This change will permit the use of pressure systems if the analysis verifies that 180°C is the minimum temperature maintained by these control systems.

7.3.6.1 For reactive substances, the heating profile may be altered for safety purposes. The decomposition is primarily controlled by maintaining the reagents at 180 ± 5°C for 9.5 minutes, therefore the time it takes to heat the samples to 180 ± 5°C is not critical. The samples may be heated at a slower rate to prevent potential uncontrollable exothermic reactions. The time to reach 180 ± 5 ºC may be increased to 10 minutes provided that 180 ± 5 ºC is subsequently maintained for 9.5 minutes. Decomposition profiles are presented in Figures 1 and 2. The extreme difference in pressure is due to the gaseous digestion products.

7.3.6.2 Calibration control is applicable in reproducing this method provided the power in watts versus time parameters are determined to reproduce the specifications listed in 7.3.6. The calibration settings will be specific to the quantity and combination of reagents, quantity of vessels, and heat loss characteristics of the vessels (Ref 1). If calibration control is being used, any vessels containing acids for analytical blank purposes are counted as sample vessels and when fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with the same acid mixture to achieve the full complement of vessels. This provides an energy balance, since the microwave power absorbed is proportional to the total absorbed mass in the cavity (Ref. 1). Irradiate each group of vessels using the predetermined calibration settings. (Different vessel types should not be mixed).

7.3.6.3 Pressure control for a specific matrix is applicable if instrument conditions are established using temperature control. Because each matrix will have a different reaction profile, performance using temperature control must be developed for every specific matrix type prior to use of the pressure control system.

7.3.7 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave system. When the vessels have cooled to near room temperature, determine if the microwave vessels have maintained a seal throughout the digestion. Due to the wide variability of vessel designs, a single procedure is not appropriate. For vessels that are sealed as discrete separate entities, the vessel weight may be taken before and after digestion to evaluate seal integrity. If the weight loss of sample exceeds 1% of the weight of the sample and reagents, then the sample is considered compromised. For vessels with burst disks, a careful visual inspection of the disk may identify compromised vessels. For vessels with resealing pressure relief mechanisms, an auditory or sometimes a physical sign indicates a vessel has vented.

7.3.8 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Vent the vessels using the procedure recommended by the vessel manufacturer. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

7.3.8.1 Centrifugation: Centrifugation at 2,000 - 3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.8.2 Settling: If undissolved material remains such as TiO_2, or other refractory oxides, allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.8.3 Filtering: If necessary, the filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.9 If the hydrofluoric acid concentration is a consideration in the analysis technique such as with ICP methods, boric acid may be added to permit the complexation of fluoride to protect the quartz plasma torch. The amount of acid added may be varied, depending on the equipment and the analysis procedure. If this option is used, alterations in the measurement procedure to adjust for the boric acid and any bias it may cause are necessary. This addition will prevent the measurement of boron as one of the elemental constituents in the sample. Alternatively, a hydrofluoric acid resistant ICP torch may be used and the addition of boric acid would be unnecessary for this analytical configuration. All major manufacturers have hydrofluoric resistant components available for the analysis of solutions containing hydrofluoric acid.

CAUTION: The traditional use of concentrated solutions of boric acid can cause problems by turning the digestion solution cloudy or result in a high salt content solution interfering with some analysis techniques. Dilute solutions of boric acid or other methods of neutralization or reagent elimination are appropriate to avoid problems with HF and the glass sample introduction devices of analytical instrumentation. Gentle heating often serves to clear cloudy solutions. Matrix matching of samples and standards will eliminate viscosity differences.

7.3.10 The removal or reduction of the quantity of the hydrochloric and hydrofluoric acids prior to analysis may be desirable. The chemistry and volatility of the analytes of interest should be considered and evaluated when using this alternative. Evaporation to near dryness in a controlled environment with controlled pure gas and neutralizing and collection of exhaust interactions is an alternative where appropriate. This manipulation may be performed in the microwave system, if the system is capable of this function, or external to the microwave system in more common apparatus(s). This option must be tested and validated to determine analyte retention and loss and should be accompanied by equipment validation possibly using the standard addition method and standard reference materials. This alternative may be used to alter either the acid concentration and/or acid composition. Note: The final solution typically requires nitric acid to maintain appropriate sample solution acidity and stability of the elements. Commonly, a 2% (v/v) nitric acid concentration is desirable. Examples of analysis performed with and without removal of the hydrofluoric acid are presented in Table 5. Waste minimization techniques should be used to capture reagent

fumes. This procedure should be tested and validated in the apparatus and on standards before using on unknown samples.

7.3.11 Transfer or decant the sample into volumetric ware and dilute the digest to a known volume. The digest is now ready for analysis for elements of interest using appropriate elemental analysis techniques and/or SW-846 methods.

7.3.12 Sample size may be scaled-up from 0.1, 0.25, or 0.5 g to 1.0 g through a series of 0.2g sample size increments. Scale-up can produce different reaction conditions and/or produce increasing gaseous reaction products. Increases in sample size may not require alteration of the acid quantity or combination, but other reagents may be added to permit a more complete decomposition and oxidation of organic and other sample constituents where necessary (such as increasing the HF for the complete destruction of silicates). Each step of the scale-up must demonstrate safe operation before continuing.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

7.5 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control to follow performance specifications of the method, then the calibration procedure will not be necessary.

7.5.1 Calibration is the normalization and reproduction of a microwave field strength to permit reagent and energy coupling in a predictable and reproducible manner. It balances reagent heating and heat loss from the vessels and is equipment dependent due to the heat retention and loss characteristics of the specific vessel. Available power is evaluated to permit the microwave field output in watts to be transferred from one microwave system to another.

Use of calibration to control this reaction requires balancing output power, coupled energy, and heat loss to reproduce the temperature heating profile in section 7.3.6. The conditions for each acid mixture and each batch containing the same specified number of vessels must be determined individually. Only identical acid mixtures and vessel models and specified numbers of vessels may be used in a given batch.

7.5.2 For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the system. The calibration format required for laboratory microwave systems depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few systems have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.5.4), otherwise, the analyst must use the multiple point calibration method (7.5.3).

7.5.3 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section 7.5.5. This data is clustered about the customary working power ranges. Nonlinearity has been encountered at the upper end of the calibration. If the system's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.5.4 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.5.5. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.5.3. This point should also be used to periodically verify the integrity of the calibration.

7.5.5 Equilibrate a large volume of water to room temperature (23 ± 2 ºC). One kg of reagent water is weighed (1,000.0 g ± 0.1 g) into a suitably inert polymeric beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2 ºC measured to ± 0.05 ºC. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the system's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05 ºC. Use a new sample for each additional measurement. If the water is reused, both the water and the beaker must have returned to 23 ± 2 ºC. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Equation 1

$$P = \frac{K \; Cp \; m \; \Delta T}{t}$$

Where:

P = the apparent power absorbed by the sample in watts (W, W = joule sec^{-1})

K = the conversion factor for thermochemical calories_sec^{-1} to watts (which equals 4.184)

Cp = the heat capacity, thermal capacity, or specific heat (cal g^{-1} $ºC^{-1}$) of water

m	=	the mass of the water sample in grams (g)
ΔT	=	the final temperature minus the initial temperature (^oC)
t	=	the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 ^oC is 0.9997 cal g^{-1} $^oC^{-1}$) the calibration equation simplifies to:

$$P = 34.86\ \Delta T$$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±5 V. Electronic components in most microwave units are matched to the system's function and output. When any part of the high voltage circuit, power source, or control components in the system have been serviced or replaced, it will be necessary to recheck the system's calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period determined by all involved parties based on program or project requirements. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples and/or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

8.4 Blank samples should be prepared using the same reagents and quantities used in sample preparation, placed in vessels of the same type, and processed with the samples.

9.0 METHOD PERFORMANCE

9.1 Precision: Precision data for Method 3052 are presented in the tables of this method. Tables 1 through 6 provide a summary of total elemental analysis.

9.2 The performance criteria are provided as an example in Figure 1. The temperature profile will be within ± 5 ^oC of the mean of the temperature profile, but the pressure curve will vary depending on the acid mixture and gaseous digestion products and the thermal insulating properties of the vessel. Figure 2 provides criteria for the digestion of an oil sample.

10.0 REFERENCES

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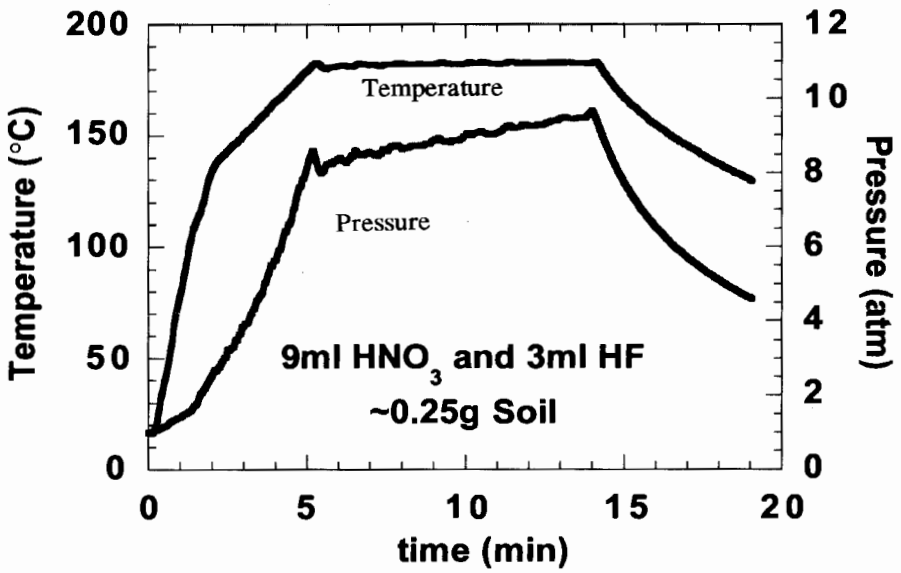


FIGURE 1. TYPICAL REACTION PROFILE FOR THE DIGESTION OF A SOIL (REF. 4 AND 8)

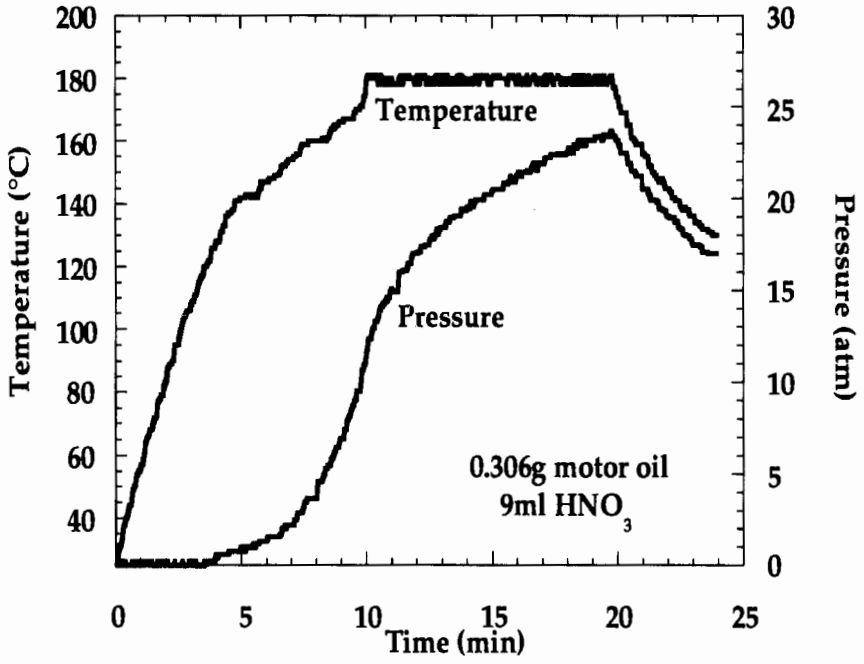


FIGURE 2. TYPICAL REACTION PROFILE FOR THE DIGESTION OF AN OIL (REF. 8)

TABLE 1
ANALYSIS OF NIST SRM 2704 (COMPILATION OF REFS. 2 AND 3)[a]
BUFFALO RIVER SEDIMENT

Element	Analyzed (µg/g)	Certified (µg/g)
Arsenic (n=4)	23.4 ± 2.6	23.4 ± 0.8
Cadmium (n=6)	3.5 ± 1.2	3.45 ± 0.22
Chromium (n=6)	132.9 ± 1.3	135 ± 5
Copper (n=6)	98.0 ± 4.2	98.6 ± 5.0
Lead (n=6)	155 ± 9.2	161 ± 17
Mercury (n=4)	1.49 ± 0.14	1.44 ± 0.07
Nickel (n=6)	43.6 ± 3.9	44.1 ± 3.0
Phosphorus (n=4)	1.016 ± 0.016 mg/g	0.998 ± 0.028 mg/g
Selenium (n=4)	1.13 ± 0.9	(1.1)
Sulfur (n=4)	3.56 ± 0.16	-----
Thallium (n=4)	1.15 ± 0.22	1.2 ± 0.2
Uranium (n=4)	2.97 ± 0.04	3.13 ± 0.13
Zinc (n=6)	441.9 ± 0.8	438 ± 12

[a] Digestion with 9 mL HNO_3 and 4 mL HF. Temperature and pressure conditions are as described in Section 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 2
ANALYSIS OF NIST SRM 2710 (REFS. 4 AND 3)[a]
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	Analyzed (µg/g)	Certified (µg/g)
Antimony	39.3 ± 0.9 [b]	38.4 ± 3.0
Cadmium	21.9 ± 0.7 [a]	21.8 ± 0.2
Chromium	34.0 ± 3.2 [b]	(39)
Copper	2902 ± 83 [a]	2950 ± 130
Lead	5425 ± 251 [a]	5532 ± 80
Nickel	13.5 ± 1.0 [a]	14.3 ± 1.0
Silver	36.6 ± 0.5 [b]	35.3 ± 1.5
Zinc	7007 ± 111 [a]	6952 ± 91

[a] Digestion with either a. 9 mL HNO_3 and 4 mL HF or b. 9 mL HNO_3, 3 mL HF, & 2 mL HCl. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 3
NIST SRM 2711 (REFS. 4 AND 3)
MONTANA SOIL: MODERATELY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	Analyzed (µg/g)	Certified (µg/g)
Cadmium	40.5 ± 1.0	41.70 ± 0.25
Chromium	45.5 ± 1.0	(47)
Copper	106.8 ± 3.4	114 ± 2
Lead	1161 ± 49	1162 ± 31
Nickel	19.6 ± 0.9	20.6 ± 1.1
Silver	4.3 ± 1.0	4.63 ± 0.39
Zinc	342 ± 9.4	350.4 ± 4.8

[a] Digestion with 9 mL HNO_3 and 4 mL HF. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 4
STABILIZATION AND RECOVERY OF ELEMENTS WITH HCl (REF. 3)[a] NIST SRM 2710
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=6)

Element	HNO_3 & HF (µg/g)	HNO_3, HF & HCl (µg/g)	Certified (µg/g)
Antimony	33.1 ± 2.1	39.3 ± 0.9	38.4 ± 3.0
Silver	10.6 ± 4.5	36.6 ± 0.5	35.3 ± 1.5

[a] HNO_3 and HF - Digestion used 9 mL and 3 mL, respectively.
HNO_3, HF, and HCl - Digestion used 9 mL, 3 mL, and 2 mL respectively. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 1. Data reported with 95% confidence intervals.

TABLE 5
FUMING OFF HYDROFLUORIC ACID WITH MICROWAVE EVAPORATION SYSTEM (REF 3)[a]
MONTANA SOIL: HIGHLY ELEVATED TRACE ELEMENT CONCENTRATIONS (n=4)

Element	Direct (µg/g)	Fumed (µg/g)	Certified (µg/g)
Antimony	39.3 ± 0.9	39.4 ± 0.9	38.4 ± 3.0
Cadmium	21.9 ± 0.7	23.3 ± 1.6	21.8 ± 0.2
Chromium	34.0 ± 3.2	32.4 ± 0.4	(39)
Copper	2902 ± 83	2870 ± 150	2950 ± 130
Lead	5425 ± 251	5502 ± 106	5532 ± 80
Nickel	13.5 ± 1.0	13.5 ± 0.8	14.3 ± 1.0
Silver	36.6 ± 0.5	38.9 ± 1.1	35.3 ± 1.5
Zinc	7007 ± 111	3992 ± 132	6952 ± 91

[a] Direct - Digestion used 9 mL HNO_3 and 3 mL HCl or 9 mL HNO_3, 3 mL HF, and 2 mL HCl
Fumed - Digestion used 9 mL HNO_3 and 3 mL HCl followed by the removal of the HF. Temperature and pressure conditions are as described in 7.3.6 of the method and similar to Figure 1. The digest solution was fumed in a microwave system under vacuum to ~1 mL and 3 mL HCl added. The digest solution was fumed to ~1 mL and 3 mL HNO_3 was added. The solution was fumed for a final step to ~1 mL and quantitatively transferred and diluted to final volume. Data reported with 95% confidence intervals.

TABLE 6
ANALYSIS OF NIST SRM 1084A (REF. 8) [a]
WEAR METALS IN OIL (100 ppm) (n=4)

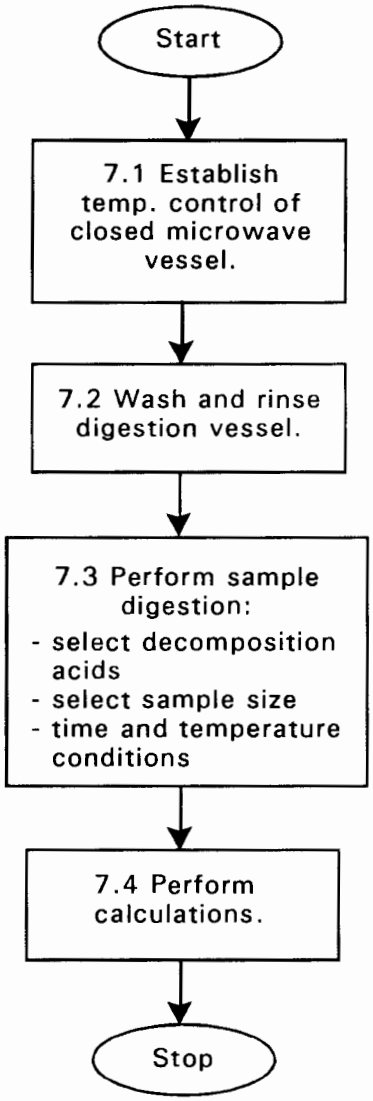
Element	Analyzed (µg/g)	Certified (µg/g)
Chromium	98.1 ± 1.1	98.3 ± 0.8
Copper	1.2.4 ± 2.4	100.0 ± 1.9
Lead	99.2 ± 2.3	101.1 ± 1.3
Nickel	99.2 ± 2.4	99.7 ± 1.6
Silver	102.7 ± 2.2	101.4 ± 1.5

[a] Digestion with 9 mL HNO_3 and 0.5 mL HF. Temperature and pressure conditions are as described in Sec. 7.3.6 of this method and similar to Figure 2. Data reported with 95% confidence intervals.

TABLE 7
DIGESTION PARAMETERS USED IN THE ANALYSIS OF SEVERAL MATRICES
BY METHOD 3052

Matrix	HNO_3	HF	HCl
Soil			
NIST SRM 2710 Highly Contaminated Montana Soil	9 mL	3 mL	0-2*mL
NIST SRM 2711 Moderately Contaminated Montana Soil	9	3	0-2*
Sediment			
NIST SRM 2704 Buffalo River Sediment	9	3	0-2*
Biological			
NIST SRM 1566a Oyster Tissue	9	0	0
NIST SRM 1577a Bovine Liver	9	0	0
Botanical			
NIST SRM 1515 Apple Leaves	9	0	0
NIST SRM 1547 Peach Leaves	9	0	0
NIST SRM 1572 Citrus Leaves	9	0.5	0
Waste Oil			
NIST SRM 1084a Wear-Metals in Lubricating Oil	9	0.5	0-2*

* HCl is added to stabilize elements such as Ag and Sb when they are analyzed.


Start
7.1 Establish temp. control of closed microwave vessel.
7.2 Wash and rinse digestion vessel.
7.3 Perform sample digestion:
- select decomposition acids
- select sample size
- time and temperature conditions
7.4 Perform calculations.
Stop

METHOD 3060A

ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM

1.0 SCOPE AND APPLICATION

1.1 Any reference in this method to “Method 3060" refers to this version of that method, and does not refer to previously published versions (e.g., in the Second Edition of this manual). When published as a new method to SW-846, a method’s number does not include a letter suffix. Each time a method is revised and made a part of SW-846 update, it receives a suffix. However, a method reference found within the text of SW-846 methods always refers to the latest version of that method published in SW-846, even if the method number at that location does not include the appropriate letter suffix.

1.2 Method 3060 is an alkaline digestion procedure for extracting hexavalent chromium [Cr(VI)] from soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments, and similar waste materials. To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied: (1) the extracting solution must solubilize all forms of Cr(VI), (2) the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III), and (3) the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI). Method 3060 meets these criteria for a wide spectrum of solid matrices. Under the alkaline conditions of the extraction, minimal reduction of Cr(VI) or oxidation of native Cr(III) occurs. The addition of Mg^{2+} in a phosphate buffer to the alkaline solution has been shown to suppress oxidation, if observed. The accuracy of the extraction procedure is assessed using spike recovery data for soluble and insoluble forms of Cr(VI) (e.g., $K_2Cr_2O_7$ and $PbCrO_4$), coupled with measurement of ancillary soil properties, indicative of the potential for the soil to maintain a Cr(VI) spike during digestion, such as oxidation reduction potential (ORP), pH, organic matter content, ferrous iron, and sulfides. Recovery of an insoluble Cr(VI) spike can be used to assess the first two criteria, and method-induced oxidation is usually not observed except in soils high in Mn and amended with soluble Cr(III) salts or freshly precipitated $Cr(OH)_3$.

1.3 The quantification of Cr(VI) in Method 3060 digests should be performed using a suitable technique with appropriate accuracy and precision, for example Method 7196 (colorimetrically by UV-VIS spectrophotometry) or Method 7199 (colorimetrically by ion chromatography (IC)). Analytical techniques such as IC with inductively coupled plasma - mass spectrometric (ICP-MS) detection, high performance liquid chromatography (HPLC) with ICP-MS detection, capillary electrophoresis (CE) with ICP-MS detection, etc. may be utilized once performance effectiveness has been validated.

2.0 SUMMARY OF METHOD

2.1 This method uses an alkaline digestion to solubilize both water-insoluble (with the exception of partial solubility of barium chromate in some soil matrices, see Reference 10.9) and water soluble Cr(VI) compounds in solid waste samples. The pH of the digestate must be carefully adjusted during the digestion procedure. Failure to meet the pH specifications will necessitate redigestion of the samples.

2.2 The sample is digested using 0.28M Na_2CO_3/0.5M NaOH solution and heating at 90-95°C for 60 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

2.3 The Cr(VI) reaction with diphenylcarbazide is the most common and reliable method for analysis of Cr(VI) solubilized in the alkaline digestate. The use of diphenylcarbazide has been well established in the colorimetric procedure (Method 7196), in rapid-test field kits, and in the ion chromatographic method for Cr(VI) (Method 7199). It is highly selective for Cr(VI) and few interferences are encountered when it is used on alkaline digestates.

2.4 For additional information on health and safety issues relating to chromium, refer to References 10.7 and 10.10.

3.0 INTERFERENCES

3.1 When analyzing a sample digest for total Cr(VI), it is appropriate to determine the reducing/oxidizing tendency of each sample matrix. This can be accomplished by characterization of each sample for additional analytical parameters, such as pH (Method 9045), ferrous iron (ASTM Method D3872-86), sulfides (Method 9030), and Oxidation Reduction Potential (ORP) (ASTM Method D 1498-93 - aqueous samples). Method 9045 (Section 7.2 of Method 9045) is referenced as the preparatory method for soil samples. The ORP and temperature probes are inserted directly into the soil slurry. The displayed ORP value is allowed to equilibrate and the resulting measurement is recorded. Other indirect indicators of reducing/oxidizing tendency include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). Analysis of these additional parameters establishes the tendency of Cr(VI) to exist or not exist in the unspiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria for total metals.

3.2 Certain substances, not typically found in the alkaline digests of soils, may interfere in the analytical methods for Cr(VI) following alkaline extraction if the concentrations of these interfering substances are high and the Cr(VI) concentration is low. Refer to Methods 7196 and 7199 for a discussion of the specific agents that may interfere with Cr(VI) quantification. Analytical techniques that reduce bias caused by co-extracted matrix components may be applicable in correcting these biases after validation of their performance effectiveness.

3.3 For waste materials or soils containing soluble Cr(III) concentrations greater than four times the laboratory Cr(VI) reporting limit, Cr(VI) results obtained using this method may be biased high due to method-induced oxidation. The addition of Mg^{2+} in a phosphate buffer to the alkaline extraction solution has been shown to suppress this oxidation. If an analytical method for Cr(VI) is used that can correct for possible method induced oxidation/reduction, then the Mg^{2+} addition is optional. The presence of soluble Cr(III) can be approximated by extracting the sample with deionized water (ASTM methods D4646-87, D5233-92, or D3987-85) and analyzing the resultant leachate for both Cr(VI) and total Cr. The difference between the two values approximates soluble Cr(III).

4.0 APPARATUS AND MATERIALS

4.1 Digestion vessel: borosilicate glass or quartz with a volume of 250 mL.

4.2 Graduated Cylinder: 100-mL or equivalent.

4.3 Volumetric Flasks: Class A glassware, 1000-mL and 100-mL, with stoppers or equivalent.

4.4 Vacuum Filtration Apparatus.

4.5 Filter membranes (0.45 µm). Preferably cellulosic or polycarbonate membranes. When vacuum filtration is performed, operation should be performed with recognition of the filter membrane breakthrough pressure.

4.6 Heating Device - capable of maintaining the digestion solution at 90-95°C with continuous auto stirring capability or equivalent.

4.7 Volumetric pipettes: Class A glassware, assorted sizes, as necessary.

4.8 Calibrated pH meter.

4.9 Calibrated balance.

4.10 Temperature measurement device (with NIST traceable calibration) capable of measuring up to 100°C (e.g. thermometer, thermistor, IR sensor, etc.).

4.11 An automated continuous stirring device (e.g. magnetic stirrer, motorized stirring rod, etc.), one for each digestion being performed.

5.0 REAGENTS

5.1 Nitric acid: 5.0 M HNO_3, analytical reagent grade or spectrograde quality. Store at 20-25°C in the dark. Do not use concentrated HNO_3 to make up 5.0 M solution if it has a yellow tinge; this is indicative of photoreduction of NO_3^- to NO_2, a reducing agent for Cr(VI).

5.2 Sodium carbonate: Na_2CO_3, anhydrous, analytical reagent grade. Store at 20-25°C in a tightly sealed container.

5.3 Sodium hydroxide: NaOH, analytical reagent grade. Store at 20-25°C in a tightly sealed container.

5.4 Magnesium Chloride: $MgCl_2$ (anhydrous), analytical reagent grade. A mass of 400 mg $MgCl_2$ is approximately equivalent to 100 mg Mg^{2+}. Store at 20-25°C in a tightly sealed container.

5.5 Phosphate Buffer:

5.5.1 K_2HPO_4: analytical reagent grade.

5.5.2 KH_2PO_4: analytical reagent grade.

5.5.3 0.5M K_2HPO_4/0.5M KH_2PO_4 buffer at pH 7: Dissolve 87.09 K_2HPO_4 and 68.04 g KH_2PO_4 into 700 mL of reagent water. Transfer to a 1L volumetric flask and dilute to volume.

5.6 Lead Chromate: $PbCrO_4$, analytical reagent grade. The insoluble matrix spike is prepared by adding 10-20 mg of $PbCrO_4$ to a separate sample aliquot. Store under dry conditions at 20-25°C in a tightly sealed container.

5.7 Digestion solution: Dissolve 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na_2CO_3 in reagent water in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle at 20-25°C and prepare fresh monthly. The pH of the digestion solution must be checked before using. The pH must be 11.5 or greater, if not, discard.

5.8 Potassium dichromate, $K_2Cr_2O_7$, spiking solution (1000 mg/L Cr(VI)): Dissolve 2.829 g of dried (105°C) $K_2Cr_2O_7$ in reagent water in a one-liter volumetric flask and dilute to the mark. Alternatively, a 1000 mg/L Cr(VI) certified primary standard solution can be used (Fisher AAS standard or equivalent). Store at 20-25°C in a tightly sealed container for use up to six months.

5.8.1 Matrix spiking solution (100 mg/L Cr(VI)): Add 10.0 mL of the 1000 mg Cr(VI)/L made from $K_2Cr_2O_7$ spiking solution (Section 5.8) to a 100 mL volumetric flask and dilute to volume with reagent water. Mix well.

5.9 Reagent Water - Reagent water will be free of interferences. Refer to Chapter One for a definition of reagent water.

6.0. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be collected using devices and placed in containers that do not contain stainless steel (e.g., plastic or glass).

6.3 Samples should be stored field-moist at 4 ± 2°C until analysis.

6.4 Hexavalent chromium has been shown to be quantitatively stable in field-moist soil samples for 30 days from sample collection. In addition, Cr(VI) has also been shown to be stable in the alkaline digestate for up to 168 hours after extraction from soil.

6.5 Hexavalent chromium solutions or waste material that are generated should be disposed of properly. One approach is to treat all Cr(VI) waste materials with ascorbic acid or other reducing agent to reduce the Cr(VI) to Cr(III). For additional information on health and safety issues relating to chromium, the user is referred to References 10.7 and 10.10.

7.0 PROCEDURE

7.1 Adjust the temperature setting of each heating device used in the alkaline digestion by preparing and monitoring a temperature blank [a 250 mL vessel filled with 50 mLs digestion solution (Section 5.7)]. Maintain a digestion solution temperature of 90-95°C as measured with a NIST-traceable thermometer or equivalent.

7.2 Place 2.5 ± 0.10 g of the field-moist sample into a clean and labeled 250 mL digestion vessel. The sample should have been mixed thoroughly before the aliquot is removed.

For the specific sample aliquot that is being spiked (Section 8.5), the spike material should be added directly to the sample aliquot at this point. (Percent solids determination, U.S. EPA CLP SOW for Organic Analysis, OLM03.1, 8/94 Rev.) should be performed on a separate aliquot in order to calculate the final result on a dry-weight basis).

7.3 Add 50 mL ± 1 mL of digestion solution (Section 5.7) to each sample using a graduated cylinder, and also add approximately 400 mg of $MgCl_2$ (Section 5.4) and 0.5 mL of 1.0M phosphate buffer (Section 5.5.3). For analytical techniques that can correct for oxidation/reduction of Cr, the addition of Mg^{2+} is optional. Cover all samples with watch glasses.

7.4 Stir the samples continuously (unheated) for at least five minutes using an appropriate stirring device.

7.5 Heat the samples to 90-95°C, then maintain the samples at 90-95°C for at least 60 minutes with continuous stirring.

7.6 Gradually cool, with continued agitation, each solution to room temperature. Transfer the contents quantitatively to the filtration apparatus; rinsing the digestion vessel with 3 successive portions of reagent water. Transfer the rinsates to the filtration apparatus. Filter through a 0.45µm membrane filter. Rinse the inside of the filter flask and filter pad with reagent water and transfer the filtrate and the rinses to a clean 250-mL vessel.

NOTE: The remaining solids and filter paper resulting from filtration of the matrix spike in Section 7.6 should be saved for possible use in assessing low Cr(VI) matrix spike recoveries. See Section 8.5.2. for additional details. Store the filtered solid at 4 ± 2°C.

7.7 Place an appropriate stirring device into the sample digest beaker, place the vessel on a stirrer, and, with constant stirring, slowly add 5.0 M nitric acid solution to the beaker dropwise. Adjust the pH of the solution to 7.5 ± 0.5 if the sample is to be analyzed using Method 7196 (adjust the pH accordingly if an alternate analytical method is to be used; i.e. 9.0 ± 0.5 if Method 7199 is to be used) and monitor the pH with a pH meter. If the pH of the digest should deviate from the desired range, discard the solution and redigest. If overshooting the desired pH range occurs repeatedly, prepare diluted nitric acid solution and repeat digestion procedure. If a flocculent precipitate should form, the sample should be filtered through a 0.45 µm membrane filter. If the filter becomes clogged using the 0.45 µm filter paper, a larger size filter paper (Whatman GFB or GFF) may be used to prefilter the samples.

CAUTION: CO_2 will be evolved. This step should be performed in a fume hood.

7.8 Remove the stirring device and rinse, collecting the rinsate in the beaker. Transfer quantitatively the contents of the vessel to a 100 mL volumetric flask and adjust the sample volume to 100 mL (to the mark for the volumetric flask) with reagent water. Mix well.

7.9 The sample digestates are now ready to be analyzed. Determine the Cr(VI) concentration in mg/kg by a suitable technique with appropriate accuracy and precision, for example Method 7196 (colorimetrically by UV-VIS spectrophotometry) or Method 7199 (colorimetrically by ion chromatography (IC)). Another analytical technique such as IC with inductively coupled plasma - mass spectrometric (ICP-MS) detection, high performance liquid chromatography (HPLC) with ICP-

MS detection, capillary electrophoresis (CE) with ICP-MS detection, etc. may be utilized once performance effectiveness has been validated.

7.10 CALCULATIONS

7.10.1 Sample Concentration

$$\text{Concentration} = \frac{A \times D \times E}{B \times C}$$

where: A = Concentration observed in the digest (µg/mL)
B = Initial moist sample weight (g)
C = % Solids/100
D = Dilution Factor
E = Final digest volume (mL)

7.10.2 Relative Percent Difference

$$RPD = \frac{(S - D)}{[(S + D)/2]}$$

where: S = Initial sample result
D = Duplicate sample result

7.10.3 Spike Recovery

$$\text{Percent Recovery} = \frac{(SSR - SR)}{SA} \times 100$$

where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

8.1 The following Quality Control (QC) analyses must be performed per digestion batch as discussed in Chapter One.

8.2 A preparation blank must be prepared and analyzed with each digestion batch, as discussed in Chapter One and detected Cr(VI) concentrations must be less than the method detection limit or one-tenth the regulatory limit or action level, whichever is greater or the entire batch must be redigested.

8.3 Laboratory Control Sample (LCS): As an additional determination of method performance, utilize the matrix spike solution prepared in Section 5.8.1 or the solid matrix spiking agent $PbCrO_4$ (Section 5.6) to spike into 50 mL of digestion solution (Section 5.7). Alternatively, the use of a certified solid reference material (if available) is recommended. Recovery must be within the certified acceptance range or a recovery range of 80% to 120% or the sample batch must be reanalyzed.

8.4 A separately prepared duplicate soil sample must be analyzed at a frequency of one per batch as discussed in Chapter One. Duplicate samples must have a Relative Percent Difference (RPD) of $\leq$ 20%, if both the original and the duplicate are $\geq$ four times the laboratory reporting limit. A control limit of ± the laboratory reporting limit is used when either the original or the duplicate sample is < four times the laboratory reporting limit.

8.5 Both soluble and insoluble pre-digestion matrix spikes must be analyzed at a frequency of one each per batch of $\leq$ 20 field samples. The soluble matrix spike sample is spiked with 1.0 mL of the spiking solution prepared in Section 5.8.1 (equivalent to 40 mg Cr(VI)/Kg)) or at twice the sample concentration, whichever is greater. The insoluble matrix spike is prepared by adding 10-20 mg of $PbCrO_4$ (Section 5.6) to a separate sample aliquot. It is used to evaluate the dissolution during the digestion process. Both matrix spikes are then carried through the digestion process described in Section 7.0. More frequent matrix spikes must be analyzed if the soil characteristics within the analytical batch appear to have significant variability based on visual observation. An acceptance range for matrix spike recoveries is 75-125%. If the matrix spike recoveries are not within these recovery limits, the entire batch must be rehomogenized/redigested/reanalyzed. If upon reanalysis, the matrix spike is not within the recovery limits, but the LCS is within criteria specified in Section 8.3, information such as that specified on Figures 1 and 2 and in Section 3.1 should be carefully evaluated . The Cr(VI) data may be valid for use despite the perceived "QC failure." The information shown on Figure 1 and discussed below is provided to interpret ancillary parameter data in conjunction with data on spike recoveries.

8.5.1 First measure the pH (Method 9045) and Oxidation Reduction Potential (ORP) (ASTM Method D 1498-93 - aqueous samples, Method 9045 preparatory for soil samples), in the field if possible. If not possible, the measurements are to be made in the laboratory prior to the determination of the spike recovery data. When and where the measurements are taken must be noted by the analyst. Adjust the ORP measurement based on reference electrode correction factor to yield Eh values. The pH and Eh values should be plotted on Figure 2 in order to give an initial indication of the sample's reducing/oxidizing nature. Upon completion of the analysis of the analytical batch, the LCS should be evaluated. If the LCS is not within 80 - 120% recovery or the certified acceptance range, then the entire analytical batch (plus the QC samples) should be redigested and reanalyzed. If the LCS was within acceptance criteria and the pre-digestion matrix spike recoveries for Cr(VI) were less than the acceptance range minimum (75%), this indicates that the soil samples reduced Cr(VI) (e.g., anoxic sediments), and no measurable native Cr(VI) existed in the unspiked sample (assuming the criteria in Section 8.3 are met). Such a result indicates that the combined and interacting influences of ORP, pH and reducing agents (e.g., organic acids, Fe^{2+} and sulfides) caused reduction of Cr(VI) spikes. Characterize each matrix spike sample for additional analytical parameters, such as ferrous iron (ASTM Method D3872-86), and sulfides (Method 9030). Laboratory measurements of pH and ORP should also be performed to confirm the field measurements. Other indirect indicators of reducing/oxidizing tendency include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biological Oxygen Demand (BOD). Analysis of these additional parameters assists in evaluating the tendency of Cr(VI)

to exist or not exist in the unspiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria for total metals.

A value of Eh-pH below the bold diagonal line on Fig. 2 indicates a reducing soil for Cr(VI). The downward slope to the right indicates that the Eh value, at which Cr(VI) is expected to be reduced, decreases with increasing pH. The solubility and quantity of organic constituents influence reduction of Cr(VI). The presence of H_2S or other strong odors indicates a reducing environment for Cr(VI). In general, acidic conditions accelerate reduction of Cr(VI) in soils, and alkaline conditions tend to stabilize Cr(VI) against reduction. If pre-digestion matrix spike recovery is not within the recovery limits, the reductive nature of the sample must be documented. This is done by plotting the Eh and pH data on the Eh-pH diagram (Fig. 2) to see if spike recovery is or is not expected in the soil. If the data point falls below the Cr(VI)-Cr(III) line on the diagram, then the data is not qualified or rejected. The sample is reducing for Cr(VI). If the data point falls above the line, then the sample is capable of supporting Cr(VI). In this case, technical error may be responsible for the poor spike recovery, and the extraction should be repeated, along with the Eh and pH measurements. If re-extraction results in a poor spike recovery again, then the data is qualified. At this point, review of other soil characteristics, such as levels of pH, Eh, TOC, sulfides, Fe(II), is appropriate to understand why poor spike recovery occurred. This extra review of these soil properties is only necessary if the unspiked sample contains detectable Cr(VI).

8.5.2 If a low or zero percent pre-digestion matrix spike recovery is obtained, an alternate approach can be used to determine the potential contribution of the sample matrix to Cr(VI) reduction. This approach consists of performing a mass balance, whereby total chromium is analyzed (Method 3052) for two samples: (1) a separate unspiked aliquot of the sample previously used for spiking, and (2) the digested solids remaining after the alkaline digestion and filtration of the matrix spike (i.e., the filtered solids from the matrix spike in Section 7.6).

The difference between the total chromium measurements should be approximately equal to the amount of the spike added to the matrix spike. If the LCS (Section 8.3) met the acceptance criteria and the Cr(VI) spike is accounted for in the filtered solids as total chromium, it is likely that the reduction of the Cr(VI) to insoluble Cr(III) resulted from the reducing matrix of the original sample subjected to Cr(VI) spiking.

8.6 A post-digestion Cr(VI) matrix spike must be analyzed per batch as discussed in Chapter One. The post-digestion matrix spike concentration should be equivalent to 40 mg/kg or twice the sample concentration observed in the unspiked aliquot of the test sample, whichever is greater.

8.6.1 Dilute the sample aliquot to a minimum extent, if necessary, so that the absorbance reading for both the unspiked sample aliquot and spiked aliquot are within the initial calibration curve.

8.6.2 A guideline for the post-digestion matrix spike recovery is 85-115%. If not achieved, consider the corrective actions/guidance on data use specified in Section 8.5 or the Method of Standard Additions (MSA) as specified in Section 8.0 of Method 7000. If the MSA technique is applied post digestion and no spike is observed from the MSA, these results indicate that the matrix is incompatible with Cr(VI) and no further effort on the part of

the laboratory is required. These digestates may contain soluble reducing agents for Cr(VI), such as fulvic acids.

9.0 METHOD PERFORMANCE

9.1 A commercial laboratory analyzed soil/sediment samples containing Cr(VI) with the results found in Table 1.

10.0 REFERENCES

10.1 United States Environmental Protection Agency, 1982. Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods. SW-846, Second Edition. Office of Solid Waste and Emergency Response, Washington, D.C.

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10.13 ASTM (American Society for Testing and Materials), 1981. Standard Test Method for Single Batch Extraction Method for Waters. ASTM Designation:D5233-92.

10.14 ASTM (American Society for Testing and Materials), 1981. Standard Test Method for Shake Extraction of Solid Waste with Water. ASTM Designation:D3987-85.

10.15 U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Multimedia Multiconcentration Document, OLM03.1, 8/94 Rev.

TABLE 1
SINGLE LABORATORY METHOD EVALUATION DATA

Sample Type	Eh (mV)[b]	pH[d]	S^{2-} (ppm)[c]	Mean Native Cr(VI) Conc. (mg/kg)	Mean Cr(VI) Spike Conc. (mg/kg)	Matrix Spike Recovery Range,%
COPR[a]/Soil Blends	550	7.4	<10.0	4.1	42.0	89.8-116
Loam	620	6.4	<10.0	ND	62.5	65.0-70.3
Clay	840	3.0	<10.0	ND	63.1	37.8-71.1
COPR[a]	460	7.4	<10.0	759	813	85.5-94.8
Anoxic Sediment	-189	7.2	25.0	ND	381	0
Quartz Sand	710	5.3	<10.0	ND	9.8	75.5-86.3

Source: Reference 10.3

Notes:

ND - Not detected
a - COPR - chromite ore processing residue
b - Corrected for the reference electrode, laboratory field moist measurement
c - Field measurement
d - Laboratory field moist measurement

FIGURE 1
QUALITY CONTROL FLOW CHART

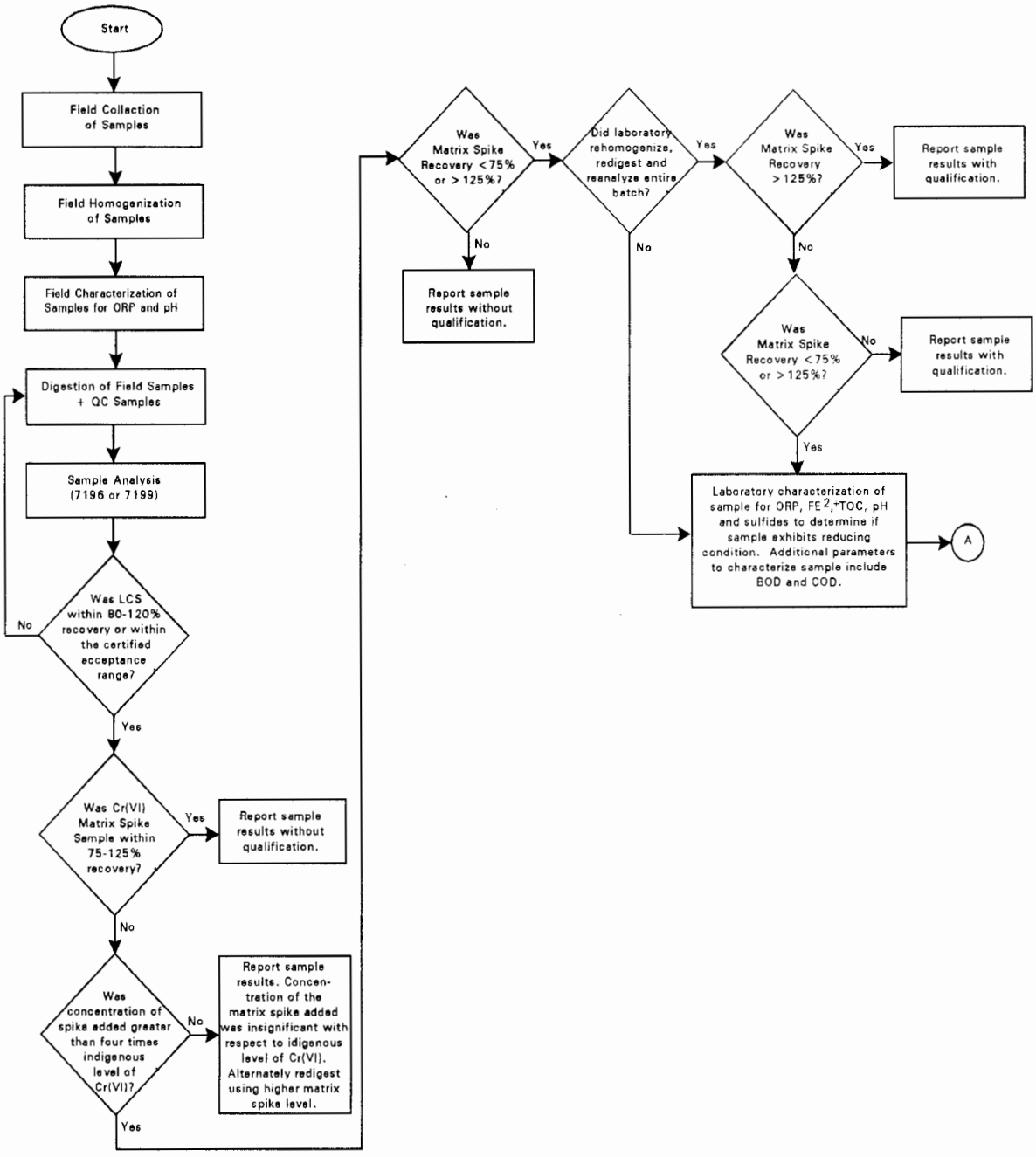


FIGURE 1
QUALITY CONTROL FLOW CHART (Continued)

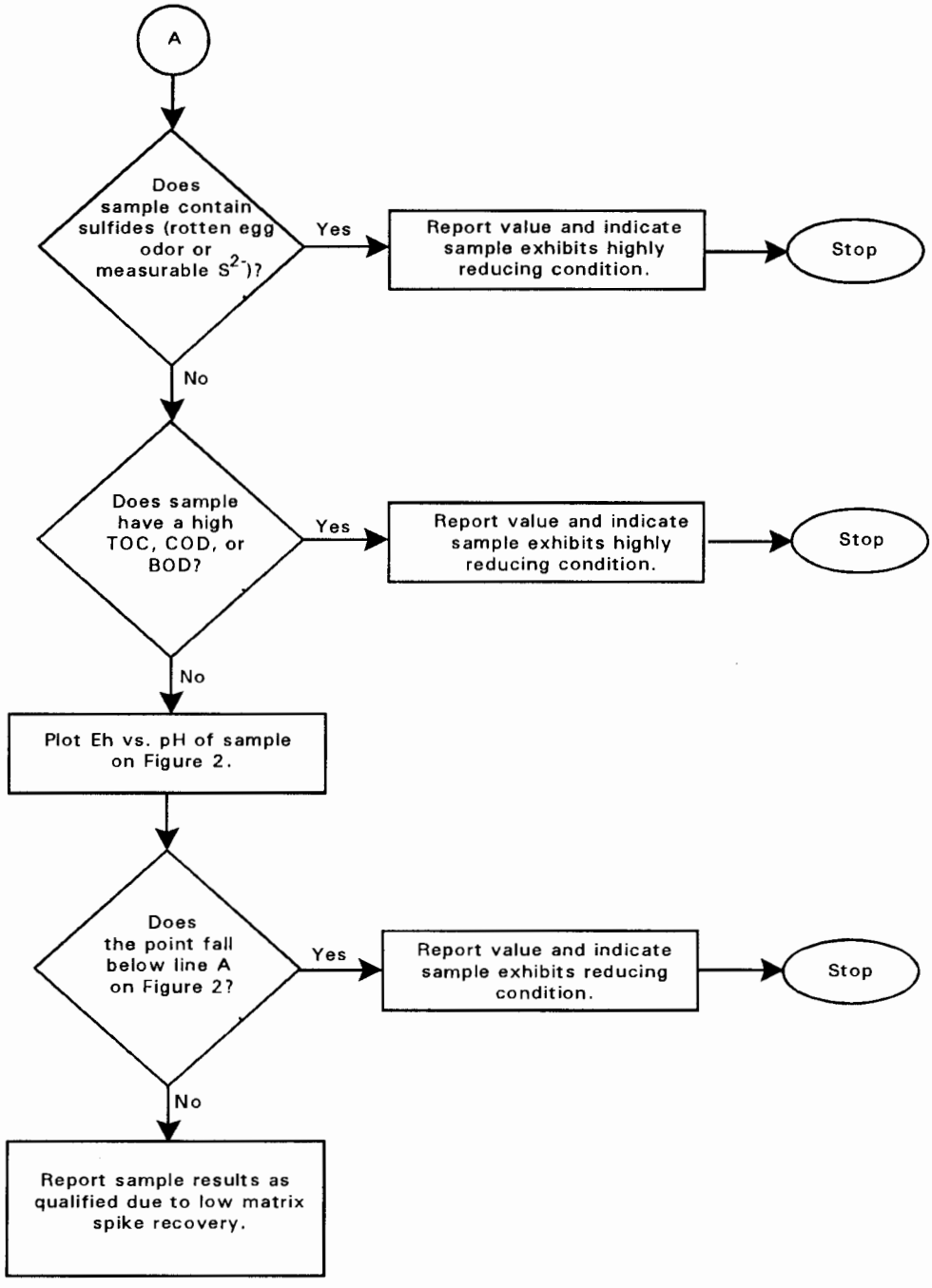
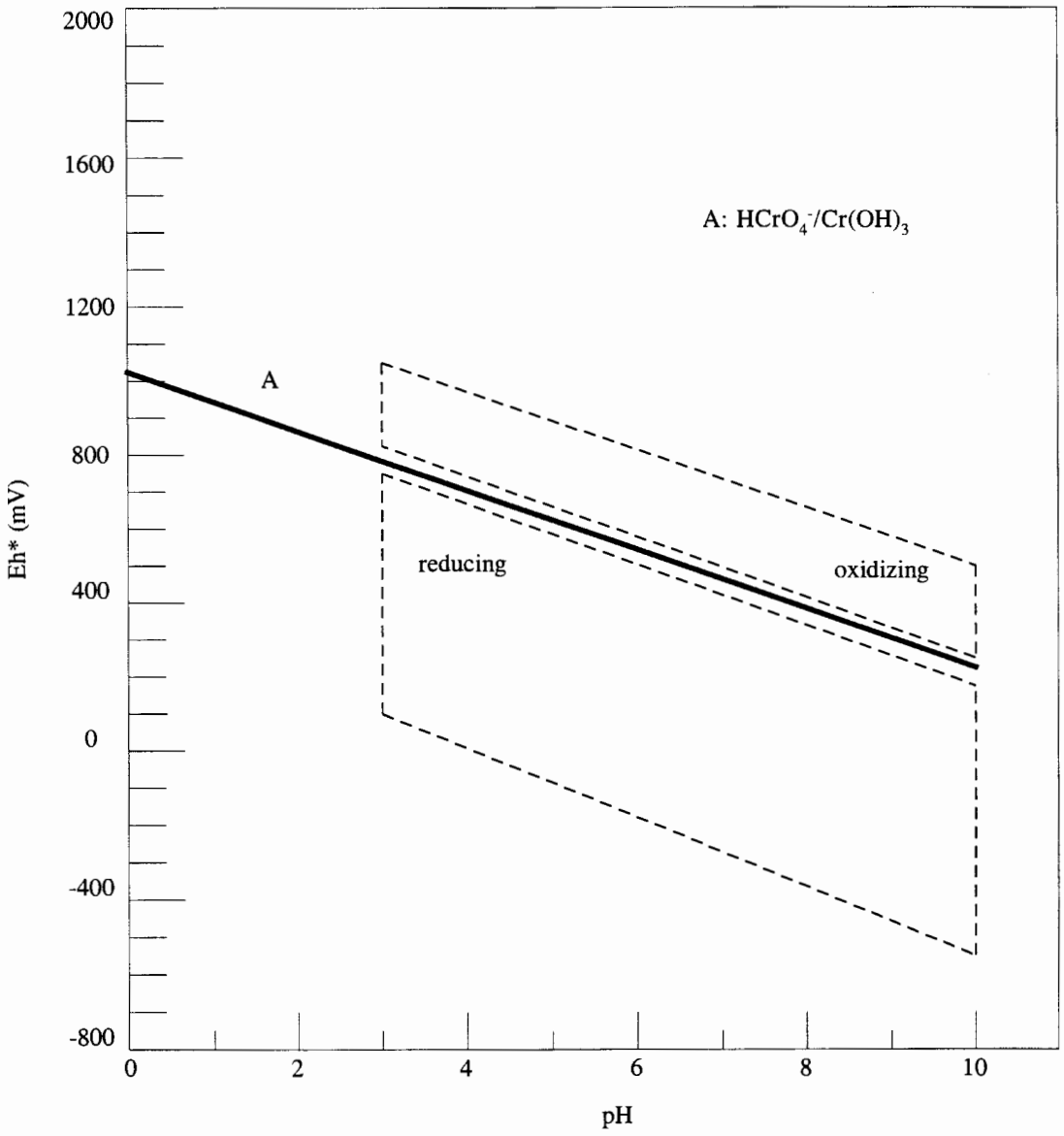


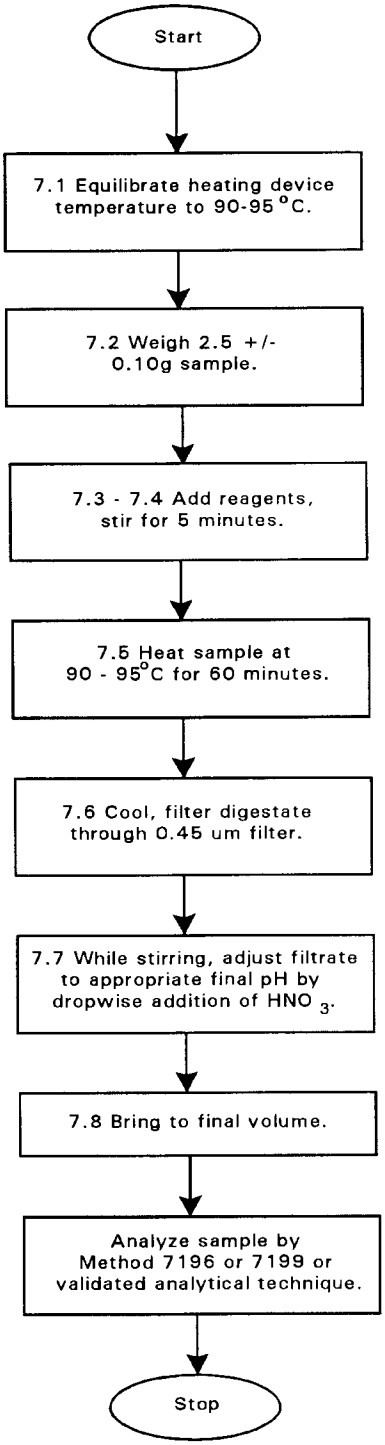
FIGURE 2
Eh/pH PHASE DIAGRAM

The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.

ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM



METHOD 3500B

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 Method 3500 provides general guidance on the selection of methods used in the quantitative extraction (or dilution) of samples for analysis by one of the semivolatile or nonvolatile determinative methods. Cleanup and/or analysis of the resultant extracts are described in Chapter Two as well as in Method 3600 (Cleanup) and Method 8000 (Analysis).

1.2 The following table lists the extraction methods, the matrix and the analyte category.

SAMPLE EXTRACTION METHODS FOR SEMIVOLATILES AND NONVOLATILES

Method #	Matrix	Extraction Type	Analytes
3510	Aqueous	Separatory Funnel Liquid-Liquid Extraction	Semivolatile & Nonvolatile Organics
3520	Aqueous	Continuous Liquid-Liquid Extraction	Semivolatile & Nonvolatile Organics
3535	Aqueous	Solid-Phase Extraction (SPE)	Semivolatile & Nonvolatile Organics
3540	Solids	Soxhlet Extraction	Semivolatile & Nonvolatile Organics
3541	Solids	Automated Soxhlet Extraction	Semivolatiles & Nonvolatile Organics
3542	Air Sampling Train	Separatory Funnel & Soxhlet Extraction	Semivolatile Organics
3545	Solids	Pressurized Fluid Extraction (ASE) (Heat & Pressure)	Semivolatile & Nonvolatile Organics
3550	Solids	Ultrasonic Extraction	Semivolatile & Nonvolatile Organics
3560/ 3561	Solids	Supercritical Fluid Extraction (SFE)	Semivolatile Petroleum Hydrocarbons & Polynuclear Aromatic Hydrocarbons
3580	Non-aqueous Solvent Soluble Waste	Solvent Dilution	Semivolatile & Nonvolatile Organics

1.3 Method 3580 may be used for the solvent dilution of non-aqueous semivolatile and nonvolatile organic samples prior to cleanup and/or analysis.

1.4 Methods 3545, 3560, and 3561 are techniques that utilize pressurized solvent extraction to reduce the amount of solvent needed to extract target analytes and reduce the extraction time when compared to more traditional techniques such as Soxhlet extraction.

1.5 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

2.0 SUMMARY OF METHOD

2.1 A sample of a known volume or weight is extracted with solvent or diluted with solvent. Method choices for aqueous samples include liquid-liquid extraction by separatory funnel or by continuous extractor and solid-phase extraction (SPE). Method choices for soil/sediment and solid waste samples include standard solvent extraction methods utilizing either Soxhlet, automated Soxhlet, or ultrasonic extraction. Solids may also be extracted using pressurized extraction techniques such as supercritical fluid extraction or heated pressurized fluid extraction.

2.2 The resultant extract is dried and concentrated in a Kuderna-Danish (K-D) apparatus. Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative methods are met (Method 8000, Sec. 8.0).

NOTE: Solvent recovery apparatus is recommended for use in methods that require the use of Kuderna-Danish evaporative concentrators. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program.

2.3 See Sec. 7.0 for additional guidance to assist in selection of the appropriate method.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures and to Chapter Four for guidance on the cleaning of glassware.

3.2 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

3.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.4 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500-mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

4.2 Solvent recovery apparatus is recommended for use in methods that require the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Stock standards for spiking solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. The stock solutions used for the calibration standards are acceptable (dilutions must be made in a water miscible solvent) except for the quality control check sample stock concentrate which must be prepared independently to serve as a check on the accuracy of the calibration solution.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in a water miscible solvent (i.e., methanol, acetone, 2-propanol, etc.) and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially-prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Stock standard solutions should be stored in polytetrafluoroethylene (PTFE)-sealed containers at 4°C or below. The solutions should be checked frequently for stability. Refer to the determinative method for holding times of the stock solutions.

5.4 Surrogate standards - A surrogate (i.e., a compound that is chemically similar to the analyte group but is not expected to occur in an environmental sample) should be added to each sample, blank, laboratory control sample (LCS), and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits.

5.4.1 Recommended surrogates for certain analyte groups are listed in Table 1. For methods where no recommended surrogates are listed, the lab is free to select compounds that fall within the definition provided above. Even compounds that are on the method target analyte list may be used as a surrogate as long as historical data are available to ensure their absence at a given site. Normally one or more standards are added for each analyte group.

5.4.2 Prepare a surrogate spiking concentrate by mixing stock standards prepared above and diluting with a water miscible solvent. Commercially prepared spiking solutions are acceptable. The concentration for semivolatile/nonvolatile organic and pesticide analyses should be such that a 1-mL aliquot into 1000 mL of a sample provides a concentration of 10 times the quantitation limit or near the mid-point of the calibration curve. Where volumes of less than 1000 mL are extracted, adjust the volume of surrogate standard proportionately. For matrices other than water, 1 mL of surrogate standard is still the normal spiking volume. However, if gel permeation chromatography will be used for sample cleanup, 2 mL should be added to the sample. See Table 1 for recommended surrogates. The spiking volumes are normally listed in each extraction method. Where concentrations are not listed in a method, a concentration of 10 times the quantitation limit is recommended. If the surrogate quantitation limit is unknown, the average quantitation limit of method target analytes may be utilized to estimate a surrogate quantitation limit. As necessary or appropriate to meet project objectives, the surrogates listed in Table 1 may be modified by the laboratory. The concentration of the surrogate in the sample (or sample extract) should either be near the middle of the calibration range or approximately ten times the quantitation limit.

5.5 Matrix spike standards - The following are recommended matrix spike standard mixtures for a few analyte groups. Prepare a matrix spike concentrate by mixing stock standards prepared above and diluting with a water miscible solvent. Commercially-prepared spiking solutions are acceptable. The matrix spike standards should be independent of the calibration standard. A few methods provide guidance on concentrations and the selection of compounds for matrix spikes (see Table 2).

5.5.1 Base/neutral and acid matrix spiking solution - Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 mg/L and the acid compounds at 200 mg/L for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.5.2 Organochlorine pesticide matrix spiking solution - Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations listed for water and sediment/soil. The concentration should be five times higher for waste samples.

Pesticide	Concentration (mg/L)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

5.5.3 For methods with no guidance, select five or more analytes (select all analytes for methods with five or less) from each analyte group for use in a spiking solution. Where matrix spike concentrations in the sample are not listed it should be at or below the regulatory concentration or action level, or 1 to 5 times higher than the background concentration, whichever, concentration would be larger.

5.5.4 Sec. 8.3.3 provides guidance on determining the concentration of the matrix spike compounds in the sample. As necessary or appropriate to meet project objectives, the matrix spiking compounds listed in Secs. 5.5.1, 5.5.2, and/or the concentrations listed in the spiking solutions may be modified by the laboratory. When the concentration of an analyte is not being checked against a regulatory limit or action level (see Sec. 8.3.3.3) the concentration of the matrix spike compound in the sample (or sample extract) should be near the middle of the calibration range or approximately ten times the quantitation limit.

5.6 Laboratory control spike standard - Use the matrix spike standard prepared in Sec. 5.5 as the spike standard for the laboratory control sample (LCS). The LCS should be spiked at the same concentration as the matrix spike.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See Chapters Two and Four for guidance on sample collection.

7.0 PROCEDURE

7.1 Water, soil/sediment, sludge, and waste samples requiring analysis for semivolatile and nonvolatile organic compounds (within this broad category are special subsets of analytes, i.e., the different groups of pesticides, explosives, PCBs etc.), must undergo solvent extraction prior to analysis. This manual contains method choices that are dependent on the matrix, the physical properties of the analytes, the sophistication and cost of equipment available to a given laboratory, and the turn-around time required for sample preparation.

7.1.1 The laboratory should be responsible for ensuring that the method chosen for sample extraction will provide acceptable extraction efficiency for the target analytes in a given matrix. There are several approaches that may be employed to ensure the appropriateness of the extraction method.

7.1.1.1 Prior to employing any extraction procedure on samples submitted for regulatory compliance monitoring purposes, the laboratory should complete the initial demonstration of proficiency described in Sec. 8.2. This demonstration applies to all SW-846 extraction methods, including those for which specific performance data are provided in a determinative method.

7.1.1.2 In addition, when a new or different extraction technique is to be applied to samples, the laboratory should also demonstrate that their application of the technique provides acceptable performance in the matrix of interest for the analytes of interest. One approach to demonstrating extraction method performance is to make a direct comparison between the chosen method and either Method 3520 (continuous liquid-liquid extraction of aqueous samples) or Method 3540 (Soxhlet extraction of solid samples), as these methods have the broadest applicability to environmental matrices.

When direct comparisons are performed, they should be conducted using either standard reference materials derived from real-world matrices or samples from a given site that can be reasonably expected to contain the analytes of interest. Because of concerns with the incorporation of spiking materials into samples, the use of samples spiked by the laboratory is generally a less useful comparison relative to either real-world contaminated samples or standard reference materials, and thus should generally only be employed when neither of these latter materials are available. Analyze at least four portions of a well homogenized sample by the extraction method of interest and either Method 3520 or Method 3540, depending on the matrix.

7.1.1.3 When direct comparisons between methods are conducted, the laboratory may use statistical tests such as an F-test to determine if the results are comparable between the methods. The laboratory may employ the method of interest provided that the demonstrated performance can be shown to be either as good or better than that of the "reference" method, or adequate for project needs, that is, meeting the requirements of the QA Project Plan for a specific project.

7.1.1.4 Whatever approaches are taken to ensure the adequacy of the extraction procedure for the matrix of interest, it is the responsibility of the laboratory to document the results and maintain records of such demonstrations.

7.1.2 Each method has QC requirements that normally include the addition of surrogates to each analytical sample and QC sample as well as the inclusion of a matrix spike/matrix spike duplicate (or matrix spike and duplicate sample), a laboratory control sample, and a method blank in each sample extraction batch. As defined in Chapter One, a "batch" consists of up to 20 environmental samples processed as a unit. In the case of samples that must undergo extraction prior to analysis, each group of 20 samples extracted together by the same method constitutes an extraction batch.

The decision of whether to prepare and analyze a matrix spike/matrix spike duplicate pair or a matrix spike and a duplicate sample should be based on knowledge of the samples in the extraction batch. If the samples are expected to contain the analytes of interest, then the analysis of a duplicate sample may yield data on the precision of the analytical process and the analysis of the matrix spike will yield data on the accuracy of the process. In contrast, when the samples are not known or expected to contain the analytes of interest, then the batch should include a matrix spike/matrix spike duplicate pair to ensure that both accuracy and precision data will be generated within the extraction batch.

7.2 Method 3510 - Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Separatory funnel extraction utilizes relatively inexpensive glassware and is fairly rapid (three, 2-minute extractions followed by filtration) but is labor intensive, uses fairly large volumes of solvent and is subject to emulsion problems. Method

3520 should be used if an emulsion forms between the solvent-sample phases, which cannot be broken by mechanical techniques.

7.3 Method 3520 - Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Continuous extractors are excellent for samples with particulates (of up to 1% solids) that cause emulsions, provide more efficient extraction of analytes that are more difficult to extract and once loaded, require no hands-on manipulation. However, they require more expensive glassware, use fairly large volumes of solvent and extraction time is rather lengthy (6 to 24 hours).

7.4 Method 3535 - Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of water is pumped through an appropriate medium (e.g., disk or cartridge) containing a solid phase that effects the extraction of organics from water. A small volume of extraction solvent is passed through the medium to elute the compounds of interest. The eluant is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Appropriate solid-phase extraction media allow extraction of water containing particulates, are relatively fast and use small volumes of solvent. However, they do require some specialized pieces of equipment.

7.5 Method 3540 - This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Soxhlet extraction uses relatively inexpensive glassware, once loaded requires no hands-on manipulation, provides efficient extraction, but is rather lengthy (16 to 24 hours) and uses fairly large volumes of solvent. It is considered a rugged extraction method because there are very few variables that can adversely affect extraction efficiency.

7.6 Method 3541 - This method utilizes a modified Soxhlet extractor and is applicable to the extraction of semivolatile/nonvolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in an automated Soxhlet extractor. This device allows the extraction thimble to be lowered into the boiling liquid for the first hour and then extracted in the normal thimble position for one additional hour. The automated Soxhlet allows equivalent extraction efficiency in 2 hours, combines the concentration step within the same device but requires a rather expensive device.

7.7 Method 3542 - This method is applicable to the extraction of semivolatile organic compounds from the Method 0010 air sampling train. The solid trapping material (i.e., glass or quartz fiber filter and porous polymeric adsorbent resin) are extracted using Soxhlet extraction and the condensate and impinger fluid are extracted using separatory funnel extraction.

7.8 Method 3545 - This method is applicable to the extraction of nonvolatile/semivolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction cell and extracted under pressure with small volumes of solvent. The extract is concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The method is rapid and efficient, in that it uses small volumes of solvent, but does require the use of an expensive extraction device.

7.9 Method 3550 - This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of ultrasonic extraction. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using ultrasonic extraction. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Ultrasonic extraction is fairly rapid (three, 3-minute extractions followed by filtration) but uses relatively large volumes of solvent, requires a somewhat expensive device and requires following the details of the method very closely to achieve acceptable extraction efficiency (proper tuning of the ultrasonic device is very critical). This technique is much less efficient than the other extraction techniques described in this section. This is most evident with very non-polar organic compounds (e.g., PCBs, etc.) that are normally strongly adsorbed to the soil matrix. EPA has not validated Method 3550 for the extraction of organophosphorus compounds from solid matrices. In addition, there are concerns that the ultrasonic energy may lead to breakdown of some organophosphorus compounds (see Reference 1). As a result, this extraction technique should not be used for organophosphorous compounds without extensive validation on real-world samples. Such studies should assess the precision, accuracy, ruggedness, and sensitivity of the technique relative to the appropriate regulatory limits or project-specific concentrations of interest.

7.10 Methods 3560 and 3561 - These methods are applicable to the extraction of total recoverable petroleum hydrocarbons and PAHs from solids such as soils, sludges, and wastes using the technique of supercritical fluid extraction (SFE). SFE normally uses CO_2 (which may contain very small volumes of solvent modifiers). Therefore, there is no solvent waste for disposal, may be automated, provides relatively rapid extraction, but, is currently limited to total recoverable petroleum hydrocarbons and PAHs. It also requires a rather expensive device and sample size is more limited. Research on SFE is currently focusing on optimizing supercritical fluid conditions to allow efficient extraction of a broader range of RCRA analytes in a broad range of environmental matrices.

7.11 Method 3580 - This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent. When using this method, the analyst must use caution in the addition of surrogate compounds, so as not to dilute out the surrogate response when diluting the sample.

7.12 Sample analysis - Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. Samples prepared for semivolatile/nonvolatile analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures. Each laboratory using SW-846 methods should maintain a formal quality assurance program. Each extraction batch of 20 or less samples should contain: a method blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate samples; and a laboratory control sample, unless the determinative method provides other guidance.

8.2 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean reference matrix. This will include a combination of the sample extraction method (usually a 3500 series method for extractable

organics) and the determinative method (an 8000 series method). The laboratory should also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made.

8.2.1 The reference samples are prepared from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the reference sample concentrate should be made using stock standards prepared independently from those used for calibration.

8.2.2 The procedure for preparation of the reference sample concentrate is dependent upon the method being evaluated. Guidance for reference sample concentrations for certain methods are listed below. In other cases, the determinative methods contain guidance on preparing the reference sample concentrate and the reference sample. If no guidance is provided, prepare a reference sample concentrate in methanol (or other water miscible solvent). Spike the reference sample at the concentration on which the method performance data are based. The spiking volume added to water should not exceed 1 mL/L so that the spiking solvent will not decrease extraction efficiency. If the method lacks performance data, prepare a reference standard concentrate at such a concentration that the spike will provide a concentration in the clean matrix that is 10 - 50 times the MDL for each analyte in that matrix.

The concentration of target analytes in the reference sample may be adjusted to more accurately reflect the concentrations that will be analyzed by the laboratory. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 8.3.1 for information on selecting an appropriate spiking level.

8.2.3 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Therefore, 1 mL (unless the method specifies a different volume) of the reference sample concentrate is spiked into each of four (minimum number of replicates) 1-L aliquots of organic-free reagent water (now called the reference sample), extracted as per the method. For matrices other than water or for determinative methods that specify a different volume of water, add 1.0 mL of the reference sample concentrate to at least four replicates of the volume or weight of sample specified in the method. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds) e.g., organic-free reagent water for the water matrix or sand or soil (free of organic interferences) for the solid matrix.

8.2.4 Preparation of reference samples

The following sections provide guidance on the QC reference sample concentrates for many SW-846 determinative methods. The concentration of the target analytes in the QC reference sample for the methods listed below may need to be adjusted to more accurately reflect the concentrations of interest in different samples or projects. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 8.3.3 for information on selecting an appropriate spiking level. In addition, the analyst may vary the concentration of the spiking solution and the volume of solution spiked into the sample. However, because of concerns about the effects of the spiking solution solvent on the sample, the total volume spiked into a sample should generally be held to no more than 1 mL.

8.2.4.1 Method 8041 - Phenols: The QC reference sample concentrate should contain each analyte at 100 mg/L in 2-propanol.

8.2.4.2 Method 8061 - Phthalate esters: The QC reference sample concentrate should contain the following analytes at the following concentrations in acetone: butyl benzyl phthalate, 10 mg/L; bis(2-ethylhexyl)phthalate, 50 mg/L; di-n-octyl phthalate, 50 mg/L; and any other phthalate at 25 mg/L.

8.2.4.3 Method 8070 - Nitrosamines: The QC reference sample concentrate should contain each analyte at 20 mg/L in isooctane.

8.2.4.4 Method 8081 - Organochlorine pesticides: The QC reference sample concentrate should contain each single-component analyte at the following concentrations in acetone: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 10 mg/L; and any other single-component pesticide at 2 mg/L. If the method is only to be used to analyze chlordane or toxaphene, the QC reference sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

8.2.4.5 Method 8082 - PCBs: The QC reference sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

8.2.4.6 Method 8091 - Nitroaromatics and cyclic ketones: The QC reference sample concentrate should contain each analyte at the following concentrations in acetone: each dinitrotoluene at 20 mg/L; and isophorone and nitrobenzene at 100 mg/L.

8.2.4.7 Method 8100 - Polynuclear aromatic hydrocarbons: The QC reference sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L; acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene 5 mg/L; and any other PAH at 10 mg/L.

8.2.4.8 Method 8111 - Haloethers: The QC reference sample concentrate should contain each analyte at a concentration of 20 mg/L in isooctane.

8.2.4.9 Method 8121 - Chlorinated hydrocarbons: The QC reference sample concentrate should contain each analyte at the following concentrations in acetone: hexachloro-substituted hydrocarbons, 10 mg/L; and any other chlorinated hydrocarbon, 100 mg/L.

8.2.4.10 Method 8131 - Aniline and selected derivatives: The QC reference sample concentrate should contain each analyte at the following concentrations in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.4.11 Method 8141 - Organophosphorus compounds: The QC reference sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.4.12 Method 8151 - Chlorinated herbicides: The QC reference sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.4.13 Method 8260 - Volatile organics: The QC reference sample concentrate should contain each analyte in methanol at a concentration of 10 mg/L. This concentrate is spiked into 100 mL of organic-free reagent water, producing enough reference sample for four aliquots of up to 25 mL each.

8.2.4.14 Method 8270 - Semivolatile organics: The QC reference sample concentrate should contain each analyte in acetone at a concentration of 100 mg/L.

8.2.4.15 Method 8310 - Polynuclear aromatic hydrocarbons: The QC reference sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L; acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene, 5 mg/L; and any other PAH at 10 mg/L.

8.2.5 Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples (Sec. 7.0 of each of the methods). This will include a combination of the sample preparation method (usually a 3500 series method for extractable organics) and the determinative method (an 8000 series method). Follow the guidance on data calculation and interpretation presented in Method 8000, Sec. 8.0.

8.2.6 The following methods contain specific extraction and sample preparation requirements applicable only to that method. Refer to these individual methods for extraction and preparation procedures required prior to instrumental analysis, and for information on the preparation of QC reference samples.

8.2.6.1 Method 8275 - Thermal Extraction/Gas Chromatography/Mass Spectrometry (TE/GC/MS) for Semivolatile Organic Compounds.

8.2.6.2 Method 8280 - Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans.

8.2.6.3 Method 8290 - Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans.

8.2.6.4 Method 8318 - N-Methylcarbamates by High Performance Liquid Chromatography (HPLC).

8.2.6.5 Method 8321 - Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection.

8.2.6.6 Method 8325 - Solvent Extractable Nonvolatiles by High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry (HPLC/PB/MS).

8.2.6.7 Method 8330 - Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC).

8.2.6.8 Method 8331 - Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC).

8.2.6.9 Method 8332 - Nitroglycerine by High Performance Liquid Chromatography (HPLC) or Thin-Layer Chromatography (TLC).

8.2.6.10 Method 8410 - Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics.

8.2.6.11 Method 8430 - Bis(2-chloroethyl) ether and Hydrolysis Products by GC/FT-IR.

8.2.6.12 Method 8440 - Total Recoverable Petroleum Hydrocarbons (TRPH) by Infrared (IR) Spectrophotometry.

8.3 Sample Quality Control for Preparation and Analysis

8.3.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair per analytical batch. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. See Sec. 5.5 for additional guidance on matrix spike preparation. Sec. 8.3.3 provides guidance on establishing the concentration of the matrix spike compounds in the sample chosen for spiking. The choice of analytes to be spiked should reflect the analytes of interest for the specific project. Thus, if only a subset of the list of target analytes provided in a determinative method are of interest (e.g., Method 8270 is used for the analysis of only PAHs), then these would be the analytes of interest for the project. In the absence of project-specific analytes of interest, it is suggested that the laboratory periodically change the analytes that are spiked with the goal of obtaining matrix spike data for most, if not all, of the analytes in a given determinative method.

8.3.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume: e.g., organic-free reagent water for the water matrix or sand or soil (free of organic interferences) for the solid matrix. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.3.3 The concentration of the matrix spike sample and/or the LCS should be determined as described in the following sections.

8.3.3.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory limit or action level, the spike should be at or below the regulatory limit or action level, or 1 - 5 times the background concentration (if historical data are available), whichever concentration is higher.

8.3.3.2 If historical data are not available, it is suggested that an uncontaminated sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculation of recoveries.

8.3.3.3 If the concentration of a specific analyte in a sample is not being checked against a limit specific to that analyte, then the spike should be at the same concentration as the reference sample (Sec. 8.2.4) or 20 times the quantitation limit in

the matrix of interest. It is again suggested that a background sample of the same matrix from the site be submitted as a sample for matrix spiking purposes.

8.3.4 Analyze these QC samples (the LCS and the matrix spikes or the optional matrix duplicates) following the procedure (Sec. 7.0) of the selected determinative method. Calculate and evaluate the QC data as outlined in Sec. 8.0 of Method 8000.

8.3.5 Blanks - Use of method blanks and other blanks are necessary to track contamination of samples during the sampling and analysis processes. Refer to Chapter One for specific quality control procedures.

8.3.6 Surrogates - A surrogate is a compound that is chemically similar to the analyte group but not expected to occur in an environmental sample. Surrogate should be added to all samples when specified in the appropriate determinative method (See Table 1). See Sec. 5.4 for additional guidance on surrogates.

8.4 The laboratory must have procedures in place for documenting and charting the effect of the matrix on method performance. Refer to Chapter One and Method 8000 for specific guidance on developing method performance data.

9.0 METHOD PERFORMANCE

9.1 The recovery of surrogates is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds, when compared to laboratory control sample (LCS) recoveries, indicates the presence or absence of unusual matrix effects.

9.2 The performance of each 3500 method will be dictated by the overall performance of the sample preparation in combination with the cleanup method and/or the analytical determinative method.

10.0 REFERENCES

None required.

TABLE 1

SURROGATES FOR SW-846 CHROMATOGRAPHIC METHODS
FOR SEMIVOLATILE AND NONVOLATILE COMPOUNDS

Method Number	Technique	Suggested Surrogates*
8041	Phenols by GC	2-Fluorophenol, and 2,4,6-Tribromophenol
8061	Phthalate Esters by GC	Diphenyl phthalate, Diphenyl isophthalate, and Dibenzyl phthalate
8070	Nitrosamines by GC	None listed**
8081	Organochlorine Pesticides by GC	2,4,5,6-Tetrachloro-m-xylene, and Decachlorobiphenyl
8082	Polychlorinated Biphenyls by GC	Decachlorobiphenyl
8091	Nitroaromatics by GC	2-Fluorobiphenyl
8100	PAHs by GC	2-Fluorobiphenyl, and 1-Fluoronaphthalene
8111	Haloethers by GC	None listed**
8121	Chlorinated Hydrocarbons by GC	α,2,6-Trichlorotoluene, 2,3,4,5,6-Pentachlorotoluene, and 1,4-Dichloronaphthalene
8131	Anilines by GC	None listed**
8141	Organophosphorus Pesticides by GC	None listed**
8151	Acid Herbicides by GC	2,4-Dichlorophenylacetic acid
8270	Semivolatiles by GC/MS	Phenol-d_6, 2-Fluorophenol, 2,4,6-Tribromophenol, Nitro-benzene-d_5, 2-Fluorobiphenyl, and p-Terphenyl-d_{14}
8275	Semivolatiles by TE/GC/MS	Not listed**
8280	PCDDs and PCDFs by HRGC/LRMS	Internal standards added at time of extraction. No surrogates.
8290	PCDDs and PCDFs by HRGC/HRMS	Internal standards added at time of extraction. No surrogates.
8310	PAHs by HPLC	Decafluorobiphenyl
8318	Carbamates by HPLC	None listed**
8321	Nonvolatiles by HPLC/TS/MS or UV Detection	None listed**

Table 1 (continued)

Method Number	Technique	Suggested Surrogates*
8325	Nonvolatiles by HPLC/PB/MS or UV/Vis	Benzidine-d_8, Caffeine-$^{15}N_2$, 3,3'-Dichlorobenzidine-d_6, Bis-(perfluorophenyl)-phenylphosphine oxide
8330	Explosives by HPLC	None listed**
8331	Tetrazene by HPLC	None listed**
8332	Nitroglycerine by HPLC or TLC	None listed**
8410	GC/FT-IR for Semivolatiles	None listed**
8430	Bis(2-chloroethyl) ether and Hydrolysis Products by GC/FT-IR	None listed**
8440	Total Recoverable Petroleum Hydrocarbons by IR	None listed**

* Suggested water concentration = 10 times the quantitation limit or near the mid-point of the calibration curve. See Sec. 5.4.2.

** Surrogate compounds selected should be similar in analytical behavior to the analytes of interest, but which are not expected to be present in the sample matrix or extract.

GC = Gas Chromatography
HR = High Resolution
LR = Low Resolution
IR = Infrared
TS = Thermospray
PB = Particle Beam
MS = Mass Spectrometry
HPLC = High Performance Liquid Chromatography
PCDD = Polychlorinated Dibenzo-*p*-dioxins
PCDF = Polychlorinated Dibenzofurans
FT-IR = Fourier Transform Infrared Detector
UV = Ultraviolet
TLC = Thin-Layer Chromatography
TE = Thermal Extraction

METHOD 3510C

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel.

2.2 The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Method 3510 is preferred over Method 3520 for the analysis of these classes of compounds. However, the recovery of phenols may be optimized by using Method 3520, and performing the initial extraction at the acid pH.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

4.2 Drying column - 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom and a PTFE stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.4 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.5 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Vials - 2-mL, glass with PTFE-lined screw-caps or crimp tops.

4.8 pH indicator paper - pH range including the desired extraction pH.

4.9 Erlenmeyer flask - 250-mL.

4.10 Syringe - 5-mL.

4.11 Graduated cylinder - 1-liter.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10 N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL. Other concentrations of hydroxide solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating to 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Other concentrations of acid solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.5 Sulfuric acid solution (1:1 v/v), H_2SO_4. Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.6 Extraction/exchange solvents - All solvents must be pesticide quality or equivalent.

5.6.1 Methylene chloride, CH_2Cl_2, boiling point 39°C.

5.6.2 Hexane, C_6H_{14}, boiling point 68.7°C.

5.6.3 2-Propanol, $CH_3CH(OH)CH_3$, boiling point 82.3°C.

5.6.4 Cyclohexane, C_6H_{12}, boiling point 80.7°C.

5.6.5 Acetonitrile, CH_3CN, boiling point 81.6°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sect. 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter (nominal) of sample. Alternatively, if the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle. If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1-L with organic-free reagent water, or samples may be collected in smaller sample bottles and the whole sample used.

7.2 Pipet 1.0 mL of the surrogate spiking solution into each sample in the graduated cylinder (or sample bottle) and mix well. (See Method 3500 and the determinative method to be used for details on the surrogate standard solution and matrix spiking solution).

7.2.1 For the sample in each batch (see Chapter One) selected for use as a matrix spike sample, add 1.0 mL of the matrix spiking standard.

7.2.2 If Method 3640, Gel-Permeation Cleanup, is to be employed, add twice the volume of the surrogate spiking solution and the matrix spiking standard, since half of the extract is not recovered from the GPC apparatus. (Alternatively, use 1.0 mL of the spiking solutions and concentrate the final extract to half the normal volume, e.g., 0.5 mL instead of 1.0 mL).

7.3 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1, using 1:1 (v/v) sulfuric acid or 10 N sodium hydroxide. Lesser strengths of acid or base solution may be employed, provided that they do not result in a significant change (<1%) in the volume of sample extracted (see Secs. 5.3 and 5.5).

7.4 Quantitatively transfer the sample from the graduated cylinder (or sample bottle) to the separatory funnel. Use 60 mL of methylene chloride to rinse the cylinder (or bottle) and transfer this rinse solvent to the separatory funnel. If the sample was transferred directly from the sample bottle, refill the bottle to the mark made in Sec. 7.1 with water and then measure the volume of sample that was in the bottle.

7.5 Seal and shake the separatory funnel vigorously for 1 - 2 minutes with periodic venting to release excess pressure. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors.

7.6 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid-Liquid Extraction.

7.7 Repeat the extraction two more times using fresh portions of solvent (Secs. 7.2 through 7.5). Combine the three solvent extracts.

7.8 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Secs. 7.2 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.9 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.10 Perform the concentration (if necessary) using the Kuderna-Danish Technique (Secs. 7.11.1 through 7.11.6).

7.11 K-D technique

7.11.1 Assemble a Kuderna-Danish (K-D) concentrator (Sec. 4.3) by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.11.2 Attach the solvent vapor recovery glassware (condenser and collection device) (Sec. 4.4) to the Snyder column of the K-D apparatus following manufacturer's instructions.

7.11.3 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 - 30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.11.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.11.5 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4. Concentrate the extract, as described in Sec. 7.11.4, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.11.6 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.12 or adjusted to 10.0 mL with the solvent last used.

7.12 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.12.1) or nitrogen blowdown technique (7.12.2) is used to adjust the extract to the final volume required.

7.12.1 Micro-Snyder column technique

If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5 - 10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or the exchange solvent, and adjust the final volume as indicated in Table 1, with solvent.

7.12.2 Nitrogen blowdown technique

7.12.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent to the final volume indicated in Table 1, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce contaminants.

7.12.2.2 The internal wall of the tube must be rinsed several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.13 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a PTFE-lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

None.

TABLE 1
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

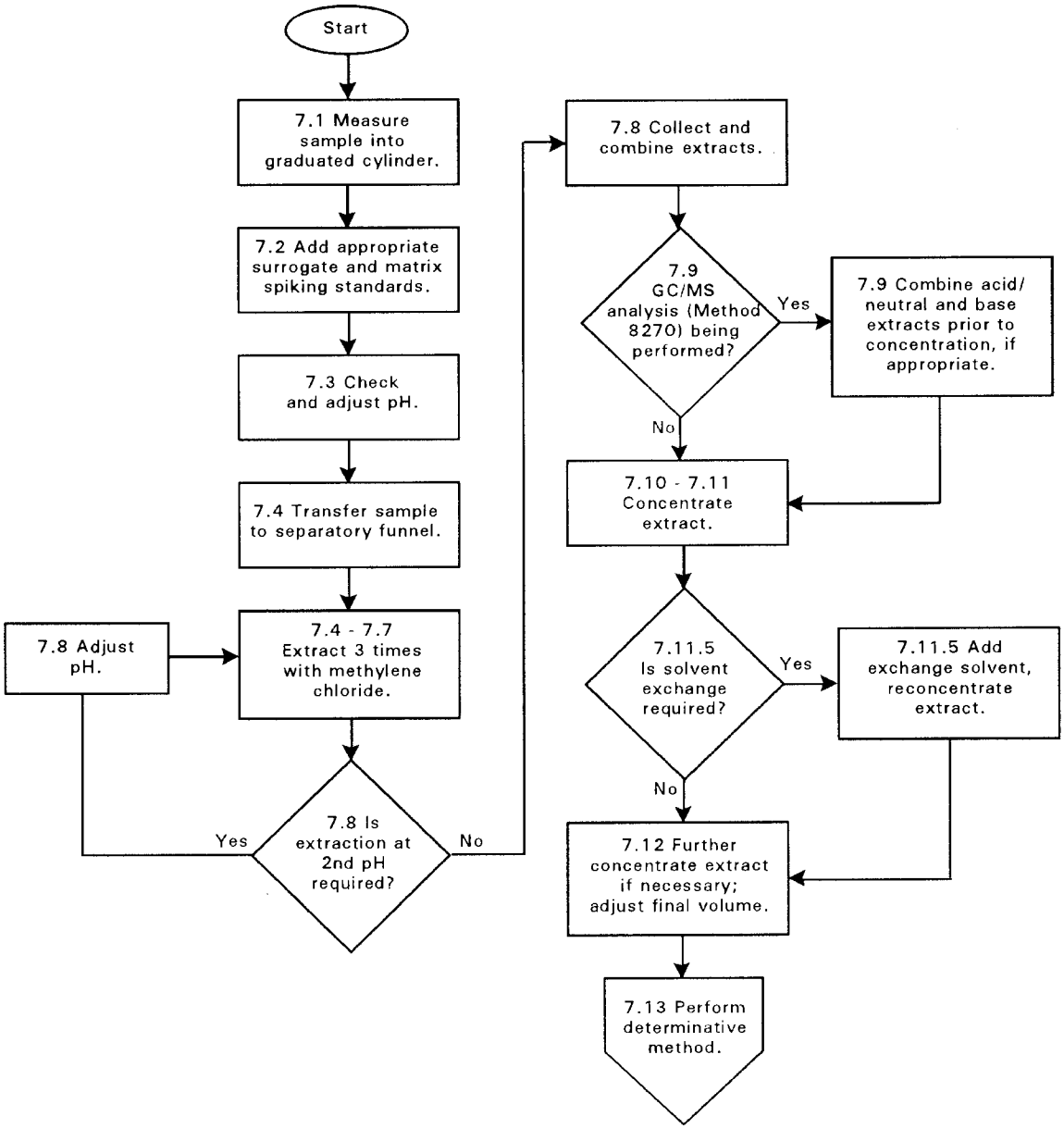
Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	≤2	none	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	5-7	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8082	5-9	none	hexane	hexane	10.0	10.0
8091	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8111	as received	none	hexane	hexane	2.0	10.0
8121	as received	none	hexane	hexane	2.0	1.0
8141	as received	none	hexane	hexane	10.0	10.0
8270[c,d]	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8325	7.0	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

[b] Phenols may be analyzed, by Method 8041, using a 1.0 mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

[d] Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Sec. 3.2).


Start
7.1 Measure sample into graduated cylinder.
7.2 Add appropriate surrogate and matrix spiking standards.
7.3 Check and adjust pH.
7.4 Transfer sample to separatory funnel.
7.4 - 7.7 Extract 3 times with methylene chloride.
7.8 Adjust pH.
7.8 Is extraction at 2nd pH required?
Yes
No
7.8 Collect and combine extracts.
7.9 GC/MS analysis (Method 8270) being performed?
Yes
7.9 Combine acid/ neutral and base extracts prior to concentration, if appropriate.
No
7.10 - 7.11 Concentrate extract.
7.11.5 Is solvent exchange required?
Yes
7.11.5 Add exchange solvent, reconcentrate extract.
No
7.12 Further concentrate extract if necessary; adjust final volume.
7.13 Perform determinative method.

METHOD 3520C

CONTINUOUS LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative steps described in Sec. 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly soluble organics in preparation for a variety of chromatographic procedures.

1.3 Method 3520 is designed for extraction solvents with greater density than the sample. Continuous extraction devices are available for extraction solvents that are less dense than the sample. The analyst must demonstrate the effectiveness of any such automatic extraction device before employing it in sample extraction.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, adjusted, if necessary, to a specific pH (see Table 1), and extracted with organic solvent for 18 - 24 hours.

2.2 The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method being employed (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The decomposition of some analytes has been demonstrated under basic extraction conditions required to separate analytes. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Method 3510 is preferred over Method 3520 for the analysis of these classes of compounds. However, the recovery of phenols may be optimized by using Method 3520 and performing the initial extraction at the acid pH.

4.0 APPARATUS AND MATERIALS

4.1 Continuous liquid-liquid extractor - Equipped with polytetrafluoroethylene (PTFE) or glass connecting joints and stopcocks requiring no lubrication (Kontes 584200-0000, 584500-0000, 583250-0000, or equivalent).

4.2 Drying column - 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom and a PTFE stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.4 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.5 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Vials - 2-mL, glass with PTFE-lined screw-caps or crimp tops.

4.8 pH indicator paper - pH range including the desired extraction pH.

4.9 Heating mantle - Rheostat controlled.

4.10 Syringe - 5-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL. Other concentrations of hydroxide solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Sulfuric acid solution (1:1 v/v), H_2SO_4. Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water. Other concentrations of acid solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.6 Extraction/exchange solvents - All solvents must be pesticide quality or equivalent.

5.6.1 Methylene chloride, CH_2Cl_2, boiling point 39°C.

5.6.2 Hexane, C_6H_{14}, boiling point 68.7°C.

5.6.3 2-Propanol, $CH_3CH(OH)CH_3$, boiling point 82.3°C.

5.6.4 Cyclohexane, C_6H_{12}, boiling point 80.7°C.

5.6.5 Acetonitrile, CH_3CN, boiling point 81.6°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter (nominal) of sample. Alternatively, if the entire contents of sample bottle are to be extracted, mark the level of sample on the outside of the bottle. If high concentrations are anticipated, a smaller sample volume may be taken and diluted to 1-L with organic-free reagent water. It is recommended that if high analyte concentrations are anticipated, samples should be collected in smaller sample bottles and the whole sample used.

7.2 Pipet 1.0 mL of the surrogate spiking solution into each sample in the graduated cylinder (or sample bottle) and mix well. (See Method 3500 and the determinative method to be used for details on the surrogate standard solution and matrix spiking solution).

7.2.1 For the sample in each batch (see Chapter One) selected for use as a matrix spike sample, add 1.0 mL of the matrix spiking standard.

7.2.2 If Method 3640, Gel-Permeation Cleanup, is to be employed, add twice the volume of the surrogate spiking solution and the matrix spiking standard, since half of the extract is not recovered from the GPC apparatus. (Alternatively, use 1.0 mL of the spiking solutions and concentrate the final extract to half the normal volume, e.g., 0.5 mL instead of 1.0 mL).

7.3 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1, using 1:1 (v/v) sulfuric acid or 10 N sodium hydroxide. Lower concentrations of acid or base solution may be employed, provided that they do not result in a significant change (<1%) in the volume of sample extracted (see Secs. 5.3 and 5.5).

7.4 Add 300 - 500 mL of methylene chloride to the distilling flask of the extractor. Add several boiling chips to the flask.

7.5 Quantitatively transfer the sample from the graduated cylinder (or sample bottle) to the extractor. Use a small volume of methylene chloride to rinse the cylinder (or bottle) and transfer this rinse solvent to the extractor. Add organic-free reagent water to the extractor, if needed, to ensure proper operation and extract for 18-24 hours. If the sample was transferred directly from the sample bottle, refill the bottle to the mark made in Sec. 7.1 with water and then measure the volume of sample that was in the bottle.

7.6 Allow the extractor to cool, then detach the boiling flask. If extraction at a secondary pH is not required (see Table 1), the extract is dried and concentrated using one of the techniques described in Secs. 7.10 - 7.11.

7.7 If a pH adjustment and second extraction is required (see Table 1), carefully, while stirring, adjust the pH of the aqueous phase to the second pH indicated in Table 1. If the extracts are to be analyzed separately (see Sec. 7.8), attach a clean distilling flask containing 500 mL of methylene chloride to the continuous extractor. Extract for 18-24 hours, allow to cool, and detach the distilling flask. If the extracts are not to be analyzed separately, then the distilling flask and solvent need not be changed and may be used for the second pH extraction.

7.8 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g., if for regulatory purposes the presence or absence of specific acid/neutral and base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.9 Perform concentration (if necessary) using the Kuderna-Danish technique (Secs. 7.10.1 through 7.10.6).

7.10 K-D technique

7.10.1 Assemble a Kuderna-Danish (K-D) concentrator (Sec. 4.3) by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.10.2 Attach the solvent vapor recovery glassware (condenser and collection device) (Sec. 4.4) to the Snyder column of the K-D apparatus following manufacturer's instructions.

7.10.3 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 - 30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.10.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.10.5 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.10.4. Concentrate the extract, as described in Sec. 7.10.4, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10.6 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the techniques outlined in Sec. 7.11 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.11.1) or nitrogen blowdown technique (7.11.2) is used to adjust the extract to the final volume required.

7.11.1 Micro-Snyder column technique

Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5 - 10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or the exchange solvent, and adjust the final volume as indicated in Table 1, with solvent.

7.11.2 Nitrogen blowdown technique

7.11.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent to the final volume indicated in Table 1, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce contaminants.

7.11.2.2 The internal wall of the tube must be rinsed several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.12 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Sec. 4.3 of this chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a PTFE-lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample-preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

None.

TABLE 1

SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

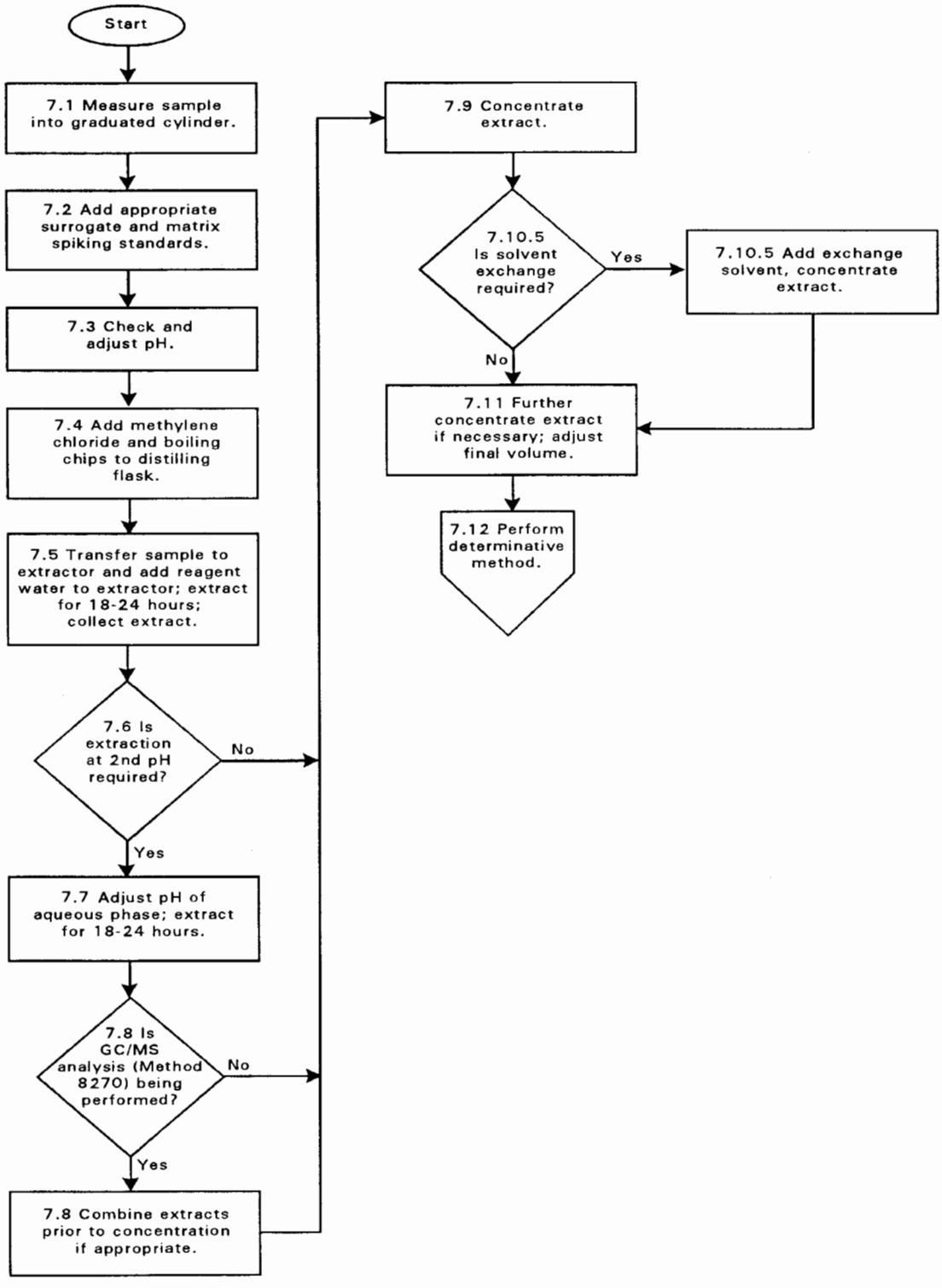
Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	≤2	none	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	5-7	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8082	5-9	none	hexane	hexane	10.0	10.0
8091	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8111	as received	none	hexane	hexane	2.0	10.0
8121	as received	none	hexane	hexane	2.0	1.0
8141	as received	none	hexane	hexane	10.0	10.0
8270[c,d]	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8325	7.0	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

[b] Phenols may be analyzed, by Method 8041, using a 1.0 mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

[d] Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Sec. 3.2).


Start
7.1 Measure sample into graduated cylinder.
7.2 Add appropriate surrogate and matrix spiking standards.
7.3 Check and adjust pH.
7.4 Add methylene chloride and boiling chips to distilling flask.
7.5 Transfer sample to extractor and add reagent water to extractor; extract for 18-24 hours; collect extract.
7.6 Is extraction at 2nd pH required?
No
Yes
7.7 Adjust pH of aqueous phase; extract for 18-24 hours.
7.8 Is GC/MS analysis (Method 8270) being performed?
No
Yes
7.8 Combine extracts prior to concentration if appropriate.
7.9 Concentrate extract.
7.10.5 Is solvent exchange required?
Yes
7.10.5 Add exchange solvent, concentrate extract.
No
7.11 Further concentrate extract if necessary; adjust final volume.
7.12 Perform determinative method.

METHOD 3535

SOLID-PHASE EXTRACTION (SPE)

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating target organic analytes from aqueous samples using solid-phase extraction media. The method describes conditions for extracting organochlorine pesticides and phthalate esters from aqueous matrices including groundwater, wastewater, and TCLP leachates using disk extraction media. Performance data for these extractions are provided in Method 8081 (organochlorine pesticides) and Method 8061 (phthalate esters). The technique may also be applicable to semivolatiles and other extractable compounds. Other solid-phase extraction media configurations, e.g., SPE cartridges, may be employed provided that the laboratory demonstrates adequate performance for the analytes of interest.

1.2 This method also provides procedures for concentrating extracts and for solvent exchange.

1.3 The method may be used for the extraction of additional target analytes or other solid-phase media if the analyst demonstrates adequate performance (e.g., recovery of 70 - 130%) using spiked sample matrices and an appropriate determinative method from Chapter Four (Sec. 4.3). Organic-free reagent water is not considered appropriate for conducting such performance studies. Specifically, many non-polar organic contaminants present in an aqueous sample are likely to be bound to particulate matter and extraction efficiencies are expected to be less than those determined from simply spiking organic-free reagent water.

1.4 Solid-phase extraction is called liquid-solid extraction (LSE) in EPA Drinking Water methods.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample is adjusted to a specified pH (see Table 1) and then extracted using a Solid-phase Extraction (SPE) device.

2.2 Target analytes are eluted from the solid-phase media using methylene chloride or other appropriate solvent. The resulting solvent extract is dried using sodium sulfate and concentrated.

2.3 The concentrated extract may be exchanged into a solvent compatible with subsequent cleanup procedures (Chapter Four, Sec. 4.2) or determinative procedures (Chapter Four, Sec. 4.3) employed for the measurement of the target analytes.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate and phthalate esters may hydrolyze. The rates of these reactions increase with increasing pH and reaction times.

3.3 Bonded phase silicas (e.g., C_{18}) will hydrolyze on prolonged exposure to aqueous samples with pH less than 2 or greater than 9. Hydrolysis will increase at the extremes of this pH range and with longer contact times. Hydrolysis may reduce extraction efficiency or cause baseline irregularities. Styrene divinylbenzene (SDB) extraction disks should be considered when hydrolysis is a problem.

3.4 Phthalates are a ubiquitous laboratory contaminant. All glass extraction apparatus should be used for this method because phthalates are used as release agents when molding rigid plastic (e.g., PVC). A method blank as described in Chapter One should be analyzed, demonstrating that there is no phthalate contamination of the sodium sulfate or other reagents specified in this method.

3.5 Sample particulates may clog the solid-phase media and result in extremely slow sample extractions. Use of an appropriate filter aid will result in shorter extractions without loss of method performance if clogging is a problem. Even when a filter aid is employed, this method may not be appropriate for aqueous samples with high levels of suspended solids (>1%), as the extraction efficiency may not be sufficient, given the small volumes of solvents employed and the short contact time.

4.0 APPARATUS AND MATERIALS

The apparatus and materials described here are based on data provided to EPA for disk-type solid-phase extraction materials. Other solid-phase extraction media configurations, e.g., SPE cartridges, may be employed provided that the laboratory demonstrates adequate performance for the analytes of interest. The use of other SPE configurations will require modifications to the procedure described in Sec. 7.0. Consult the manufacturer's instruction**s** regarding such modifications.

4.1 Solid-phase extraction system - Empore™ manifold with 3-90 mm or 6-47 mm standard filter apparatus, or equivalent. Automatic or robotic sample preparation systems designed for solid-phase media may be utilized for this method if adequate performance is achieved and all quality control requirements are satisfied.

4.1.1 Manifold station - (Fisher Scientific 14-378-1B [3-place], 14-378-1A [6-place], or equivalent).

4.1.2 Standard Filter Apparatus - (Fisher Scientific 14-378-2A [47-mm], 14-378-2B [90-mm], or equivalent), consisting of a sample reservoir, clamp, fritted disk and filtration head with drip tip.

4.1.3 Tube, collection - 60-mL (Kimble 609-58-A16, or equivalent). The collection tube should be of appropriate I.D. and length for the drip tip of the standard filter apparatus to be positioned well into the neck of the tube to prevent splattering.

4.1.4 Filter flask - 2-L with a ground glass receiver joint (Kontes K-953828-0000, or equivalent) (optional). May be used to carry out individual disk extractions with the standard filter apparatus and collection vial in an ALL GLASS SYSTEM.

4.2 Solid-phase extraction disks - Empore™, or equivalent, C_{18} disks. 47-mm and 90-mm disks are available. Solid-phases other than C_{18} may be employed, provided that adequate performance is demonstrated for the anlytes of interest.

4.3 Filtration aid (optional).

4.3.1 Filter Aid 400 - (Fisher Scientific 14-378-3, or equivalent).

4.3.2 In-situ glass micro-fiber prefilter - (Whatman GMF 150, 1 micron pore size, or equivalent).

4.4 Drying column - 22-mm ID Pyrex® chromatographic column with a polytetrafluoroethylene (PTFE) stopcock (Kontes K-420530-0242, or equivalent).

NOTE: Fritted glass discs used to retain sodium sulfate in some columns are difficult to decontaminate after contact with highly contaminated or viscous extracts. Columns suitable for this method use a small pad of Pyrex® glass wool to retain the drying agent.

4.5 Kuderna-Danish (K-D) apparatus.

4.5.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025, or equivalent). A ground-glass stopper is used to prevent evaporation of extracts during short-term storage.

4.5.2 Evaporation flask - 500-mL (Kontes K-570001-500, or equivalent). Attach to concentrator tube using springs or clamps.

4.5.3 Snyder column - Three-ball macro- (Kontes K-503000-0121, or equivalent).

4.5.4 Snyder column - Two-ball micro- (Kontes K-569001-0219, or equivalent) (optional).

4.5.5 Springs - 1/2 inch (Kontes K-662750, or equivalent).

NOTE: The glassware in Sec. 4.6 is recommended for the purpose of solvent recovery during the concentration procedures (Secs. 7.13 and 7.14.1) requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. The EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.6 Solvent Vapor Recovery System (Kontes 545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.7 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide, or equivalent).

4.8 Water bath - Heated, with concentric ring cover, capable of temperature control to ± 5°C. The bath should be used in a hood.

4.9 N-Evap - Nitrogen blowdown apparatus, 12- or 24-position (Organomation Model 112, or equivalent) (optional).

4.10 Vials, glass - Sizes as appropriate, e.g., 2-mL or 10-mL with PTFE-fluorocarbon-lined screw caps or crimp tops for storage of extracts.

4.11 pH indicator paper - Wide pH range (Fisher Scientific 14-850-13B, or equivalent).

4.12 Vacuum system - Capable of maintaining a vacuum of approximately 66 cm (26 inches) of mercury.

4.13 Graduated cylinder - Sizes as appropriate.

4.14 Pipets, disposable (Fisher Scientific 13-678-20C, or equivalent).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without decreasing the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 - Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride.

5.4 Solutions for adjusting the pH of samples before extraction.

5.4.1 Sulfuric acid solution (1:1 v/v), H_2SO_4 - Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.4.2 Sodium hydroxide solution (10N), NaOH - Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.5 Extraction, washing, and exchange solvents - All solvents must be pesticide quality or equivalent.

5.5.1 Methylene chloride, CH_2Cl_2.

5.5.2 Hexane, C_6H_{14}.

5.5.3 Ethyl acetate, $CH_3COOC_2H_5$.

5.5.4 Acetonitrile, CH_3CN.

5.5.5 Methanol, CH_3OH.

5.5.6 Acetone, $(CH_3)_2CO$.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Using a graduated cylinder, measure a 1-liter sample. Take care to minimize any loss of sample particulates during this step. This method may not be appropriate for aqueous samples with greater than 1% suspended solids, as such samples can be difficult to filter and the extraction efficiency may be reduced as a result of the small volumes of solvents employed and the short contact time. If the particulate load significantly slows or prevents filtration, it may be more appropriate to employ an alternative extraction procedure.

7.1.1 Add 5.0 mL of methanol and any surrogate standards listed in the determinative method to all samples and blanks.

7.1.2 Prepare matrix spikes by adding appropriate matrix spike standards to representative sample replicates. The frequency with which matrix spikes are prepared and analyzed is described in Chapter One or as part of the determinative method.

7.1.3 If cleanup procedures are to be employed that result in the loss of extract, adjust the amount of surrogate and spiking cocktail(s) accordingly. In the case of Method 3640, Gel Permeation Cleanup, double the amount of standards to compensate for the loss of one half of the extract concentrate when loading the GPC column.

7.1.4 If high concentrations of target analytes are anticipated to be present in samples, a smaller volume may be extracted.

7.2 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH range listed in Table 1.

CAUTION: The adjustment of the sample pH may lead to precipitation or flocculation reactions that may remove analytes from the aqueous portion of the sample. The analyst should note the formation of precipitates or floc and take care to transfer any such material to the extraction device, rinsing the graduated cylinder with organic-free reagent water, and adding the rinse to the extraction device.

7.3 Assemble a manifold for multiple extractions (Figure 1) using 47-mm or 90-mm Empore™ disks. Use a filter flask with the standard filter apparatus for single extractions. If samples contain significant quantities of particulates, the use of a filter aid or prefilter is advisable. Empore™ Filter Aid 400 or Whatman GMF 150 prefilters are recommended.

7.3.1 Pour about 40 g of Filter Aid 400 onto the surface of the disk after assembling the standard filter apparatus.

7.3.2 Place the Whatman GMF 150 on top of the Empore™ disk prior to clamping the glass reservoir into the standard filter apparatus.

7.4 Wash the extraction apparatus and disk with 20 mL of methylene chloride introduced by rinsing down the sides of the glass reservoir. Pull a small amount of solvent through the disk with a vacuum; turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry.

7.4.1 When using a filtration aid, adjust the volume of all wash solvents so the entire filtration bed is submerged.

7.4.2 In subsequent conditioning steps, volumes should be adjusted so that a level of solvent is always maintained above the entire filter bed.

7.5 Continue to wash the extraction apparatus and disk by adding 10 mL of acetone down the sides of the glass reservoir. Pull a small amount of solvent through the disk with a vacuum; turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry. When using a filtration aid, adjust the volume of acetone so that the entire filtration bed is submerged.

7.6 Pre-wet (condition) the disk by adding 20 mL of methanol to the reservoir, pulling a small amount through the disk and then letting it soak for about one minute. Pull most of the remaining methanol through the disk, leaving 3 - 5 mm of methanol above the surface of the disk. From this point until the sample extraction has been completed, the surface of the disk should not be allowed to go dry. THIS IS A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY.

7.6.1 The disk is composed of hydrophobic materials which will not pass water unless they are pre-wetted with a water-miscible solvent. Should a disk accidentally go dry during the conditioning step, the methanol pre-wetting and water washing steps must be repeated prior to adding the sample.

7.6.2 When using a filtration aid, adjust the volume of conditioning solvents so that the entire filtration bed remains submerged until the extraction is completed.

7.7 Rinse the disk by adding 20 mL of organic-free reagent water to the disk and drawing most through, leaving 3 - 5 mm of water above the surface of the disk.

7.8 Add a water sample, blank or matrix spike (Sec. 7.1) to the reservoir and, under full vacuum, filter as quickly as the vacuum will allow (at least 10 minutes). Transfer as much of the measured volume of water as possible. After the sample has passed through the solid-phase media, dry the disk by maintaining vacuum for about 3 minutes.

NOTE: If the sample contains particulate matter or sediment that is considered part of the sample, allow the sample to settle and decant as much of the liquid as practical into the reservoir. After most of the aqueous portion of the sample has passed through the disk, swirl the remaining portion of the sample to suspend the particulate matter or sediment and transfer it to the reservoir. Use additional portions of organic-free reagent water to complete the transfer. The particulates must be transferred to the reservoir before all of the aqueous sample has passed through the disk. If the particulate matter or sediment is not considered part of the sample, allow the sample to settle before measuring the aliquot in Sec. 7.1.

7.9 Remove the entire standard filter assembly (do not disassemble) from the manifold and insert a collection tube. The collection tube should have sufficient capacity to hold all of the elution solvents. The drip tip of the filtration apparatus should be seated sufficiently below the neck of the

collection tube to prevent analyte loss due to splattering when vacuum is applied. When using a filter flask for single extractions, empty the water from the flask before inserting the collection tube.

7.10 Add 5.0 mL of acetone to the disk. Allow the acetone to spread out evenly across the disk (or inert filter) then quickly turn the vacuum on and off to pull the first drops of acetone through the disk. Allow the disk to soak for 15 to 20 seconds before proceeding to Sec. 7.11.

7.10.1 The initial elution with a water-miscible solvent, i.e., acetone, improves the recovery of analytes trapped in water-filled pores of the sorbent. Use of a water-miscible solvent is particularly critical when methylene chloride is used as the second elution solvent.

7.10.2 When using a filtration aid, adjust the volume of eluting solvent so that the entire filtration bed is initially submerged.

7.11 Add 15 mL of methylene chloride (or other suitable elution solvent, see Table 1) to the sample bottle. Rinse the bottle thoroughly and, with the initial portion of acetone still on the disk, transfer the solvent to the disk with a disposable pipette, rinsing down the sides of the filtration reservoir in the process. Draw about half of the solvent through the disk and then release the vacuum. Allow the remaining elution solvent to soak the disk and particulate for about one minute before drawing the remaining solvent through the disk under vacuum. When using a filtration aid, adjust the volume of elution solvent so that the entire filtration bed is initially submerged.

7.12 Repeat Sec. 7.11 with a second 15-mL aliquot of elution solvent (see Table 1).

7.13 K-D concentration technique.

7.13.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.13.2 Dry the combined extracts in the collection tube (Secs. 7.10-7.12) by passing them through a drying column containing about 10 g of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Use acidified sodium sulfate (Method 8151) if acidic analytes are to be measured.

7.13.3 Rinse the collection tube and drying column into the K-D flask with an additional 20-mL portion of solvent in order to achieve a quantitative transfer.

7.13.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Attach the solvent vapor recovery glassware (condenser and collection device, see Sec. 4.6) to the Snyder column of the K-D apparatus, following manufacturer's instructions. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.13.4.1 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip.

7.13.4.2 Reattach the Snyder column. Concentrate the extract, raising the temperature of the water bath, if necessary, to maintain a proper distillation rate.

7.13.5 Remove the Snyder column. Rinse the K-D flask and the lower joints of the Snyder column into the concentrator tube with 1 - 2 mL of solvent. The extract may be further concentrated by using a technique outlined in Sec. 7.14 or adjusted to a final volume of 5.0 - 10.0 mL using an appropriate solvent (Table 1).

7.14 If further concentration is required, use either the micro-Snyder column technique (7.14.1) or nitrogen blowdown technique (7.14.2).

7.14.1 Micro-Snyder column technique.

7.14.1.1 Add a fresh clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column directly to the concentrator tube. Attach the solvent vapor recovery glassware (condenser and collection device) to the micro-Snyder column of the K-D apparatus, following manufacturer's instructions. Prewet the Snyder column by adding 0.5 mL of methylene chloride or the exchange solvent to the top of the column. Place the micro-concentration apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5 - 10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

7.14.1.2 When the apparent volume of liquid reaches 0.5 mL, remove the apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final extract volume to 1.0 - 2.0 mL.

7.14.2 Nitrogen blowdown technique.

7.14.2.1 Place the concentrator tube in a warm bath (30°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce phthalate interferences.

7.14.2.2 Rinse down the internal wall of the concentrator tube several times with solvent during the nitrogen blowdown. During evaporation, position the concentrator tube to avoid condensing water into the extract. Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, some semivolatile analytes such as cresols may be lost.

7.15 The extract may now be subjected to cleanup procedures or analyzed for the target analytes using the appropriate determinative technique(s). If further handling of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a PTFE-lined screw-cap, and labeled appropriately. In no case should the recommended holding times for analytical procedures provided in Chapter Four, Table 4-1 be exceeded.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for general quality control procedures and Method 3500 for specific QC procedures for extraction and sample preparation.

9.0 METHOD PERFORMANCE

Refer to the determinative methods listed in Table 1 for performance data.

10.0 REFERENCES

1. Lopez-Avila, V., Beckert, W., et. al., "Single Laboratory Evaluation of Method 8060 - Phthalate Esters", EPA/600/4-89/039.

2. Tomkins, B.A., Merriweather, R., et. al., "Determination of Eight Organochlorine Pesticides at Low Nanogram/Liter Concentrations in Groundwater Using Filter Disk Extraction and Gas Chromatography", JAOAC International, 75(6), pps. 1091-1099 (1992).

FIGURE 1
DISK EXTRACTION APPARATUS

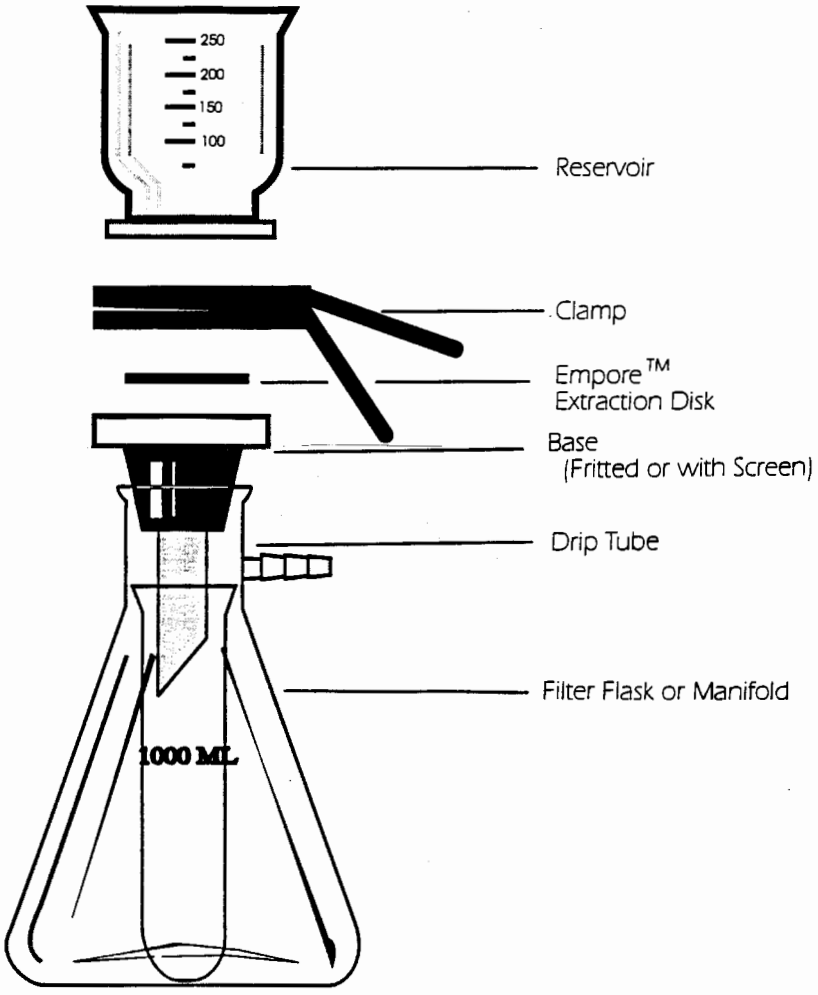
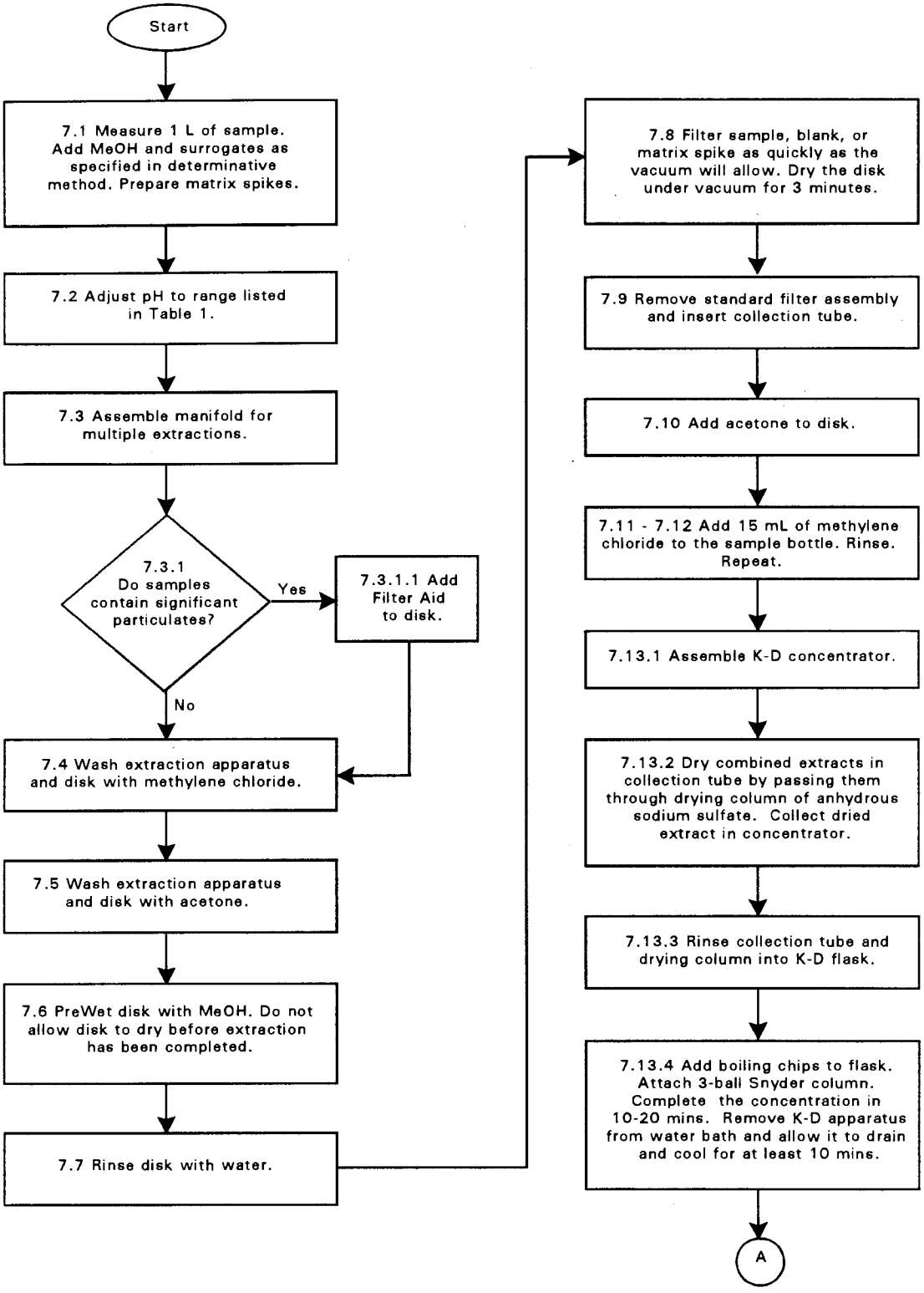
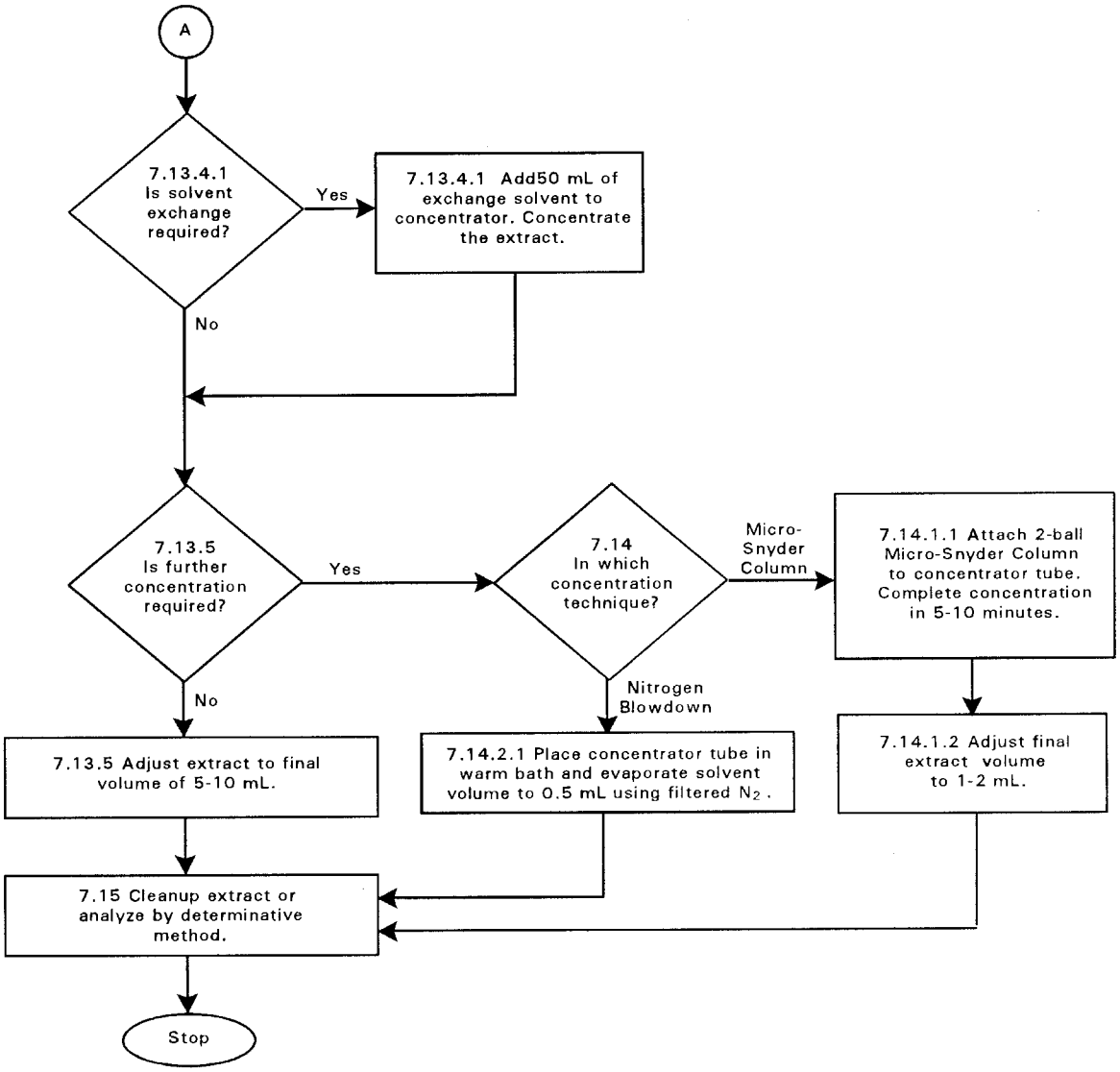


TABLE 1
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative Method	Extraction pH	Disk Medium	Elution Solvent	Exchange Solvent	Final Extract Volume for Analysis (mL)[a]
8061	5-7	C_{18}	acetonitrile	hexane	10.0
8081	5-9	C_{18}	methylene chloride	hexane	10.0
8325	7.0	C_{18}	methanol or acetonitrile	methanol	1.0

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.


Start
7.1 Measure 1 L of sample. Add MeOH and surrogates as specified in determinative method. Prepare matrix spikes.
7.2 Adjust pH to range listed in Table 1.
7.3 Assemble manifold for multiple extractions.
7.3.1 Do samples contain significant particulates?
Yes
7.3.1.1 Add Filter Aid to disk.
No
7.4 Wash extraction apparatus and disk with methylene chloride.
7.5 Wash extraction apparatus and disk with acetone.
7.6 PreWet disk with MeOH. Do not allow disk to dry before extraction has been completed.
7.7 Rinse disk with water.
7.8 Filter sample, blank, or matrix spike as quickly as the vacuum will allow. Dry the disk under vacuum for 3 minutes.
7.9 Remove standard filter assembly and insert collection tube.
7.10 Add acetone to disk.
7.11 - 7.12 Add 15 mL of methylene chloride to the sample bottle. Rinse. Repeat.
7.13.1 Assemble K-D concentrator.
7.13.2 Dry combined extracts in collection tube by passing them through drying column of anhydrous sodium sulfate. Collect dried extract in concentrator.
7.13.3 Rinse collection tube and drying column into K-D flask.
7.13.4 Add boiling chips to flask. Attach 3-ball Snyder column. Complete the concentration in 10-20 mins. Remove K-D apparatus from water bath and allow it to drain and cool for at least 10 mins.
A


A
7.13.4.1 Is solvent exchange required?
Yes
7.13.4.1 Add50 mL of exchange solvent to concentrator. Concentrate the extract.
No
7.13.5 Is further concentration required?
Yes
7.14 In which concentration technique?
Micro-Snyder Column
7.14.1.1 Attach 2-ball Micro-Snyder Column to concentrator tube. Complete concentration in 5-10 minutes.
No
Nitrogen Blowdown
7.13.5 Adjust extract to final volume of 5-10 mL.
7.14.2.1 Place concentrator tube in warm bath and evaporate solvent volume to 0.5 mL using filtered N_2.
7.14.1.2 Adjust final extract volume to 1-2 mL.
7.15 Cleanup extract or analyze by determinative method.
Stop

USEPA METHOD 3535A

SOLID-PHASE EXTRACTION (SPE)

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating target organic analytes from aqueous samples using solid-phase extraction (SPE) media. The method describes conditions for extracting a variety of organic compounds from aqueous matrices that include: groundwater, wastewater, and TCLP leachates. The method describes the use of disk extraction media for eight groups of analytes and the use of cartridge extraction media for one group of analytes. Other solid-phase extraction media may be employed as described in see Sec. 4.0. The extraction procedures are specific to the analytes of interest and vary by group of analytes and type of extraction media. The groups of analytes that have been evaluated thus far are listed below, along with the types of media that have been evaluated, and the determinative methods in which the corresponding performance data can be found.

Analyte Group	Extraction Media Type	Determinative Method
Phthalate esters	Disks	8061
Organochlorine pesticides	Disks	8081
Polychlorinated biphenyls (PCBs)	Disks	8082
Organophosphorus pesticides	Disks	8141
Nitroaromatics and nitramines	Disks and Cartridges	8330
TCLP leachates containing organochlorine pesticides	Disks	8081
TCLP leachates containing semivolatiles	Disks	8270
TCLP leachates containing phenoxyacid herbicides	Disks	8321

1.2 The technique may also be applicable to other semivolatile or extractable compounds. It may also be used for the extraction of additional target analytes or may employ other solid-phase media, provided that the analyst demonstrates adequate performance (e.g., recovery of 70 - 130%, or project-specific recovery criteria) using spiked sample matrices and an appropriate determinative method of the type included in Chapter Four (Sec. 4.3). The use of organic-free reagent water alone is not considered sufficient for conducting such performance studies, and must be supported by data from actual sample matrices.

1.3 This method also provides procedures for concentrating extracts and for solvent exchange.

1.4 Solid-phase extraction is called liquid-solid extraction in some methods associated with the Safe Drinking Water Act.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Sample preparation procedures vary by analyte group. Extraction of some groups requires that the pH of the sample be adjusted to a specified value prior to extraction (see Sec. 7.2). Other groups do not require a pH adjustment.

2.2 Following any necessary pH adjustment, a measured volume of sample is extracted by passing it through the solid-phase extraction medium (disks or cartridges), which is held in an extraction device designed for vacuum filtration of the sample.

2.3 Target analytes are eluted from the solid-phase media using an appropriate solvent (see Secs. 7.8 and 7.9) which is collected in a receiving vessel. The resulting solvent extract is dried using sodium sulfate and concentrated, as needed.

2.4 As necessary for the specific analysis, the concentrated extract may be exchanged into a solvent compatible extract with subsequent cleanup procedures (Chapter Four, Sec. 4.2) or determinative procedures (Chapter Four, Sec. 4.3) for the measurement of the target analytes.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate and phthalate esters may hydrolyze. The rates of these reactions increase with increasing pH and reaction times.

3.3 Bonded-phase silica (e.g., C_{18}) will hydrolyze on prolonged exposure to aqueous samples with pH less than 2 or greater than 9. Hydrolysis will increase at the extremes of this pH range and with longer contact times. Hydrolysis may reduce extraction efficiency or cause baseline irregularities. Styrene divinylbenzene (SDB) extraction disks should be considered when hydrolysis is a problem.

3.4 Phthalates are a ubiquitous laboratory contaminant. All glass extraction apparatus should be used for this method because phthalates are used as release agents when molding rigid plastic (e.g., PVC) and as plasticizers for flexible tubing. A method blank, as described in Chapter One, should be analyzed, demonstrating that there is no phthalate contamination of the sodium sulfate or other reagents listed in this method.

3.5 Sample particulates may clog the solid-phase media and result in extremely slow sample extractions. Use of an appropriate filter aid will result in shorter extractions without loss of method performance if clogging is a problem. Even when a filter aid is employed, this method may not be appropriate for aqueous samples with high levels of suspended solids (>1%), as the extraction efficiency may not be sufficient, given the small volumes of solvents employed and the short contact time.

4.0 APPARATUS AND MATERIALS

The apparatus and materials described here are based on data provided to EPA for the extraction of eight groups of analytes using disk-type materials and for the extraction of one group of analytes using cartridge-type materials. Other solid-phase extraction media configurations may be employed, provided that the laboratory demonstrates adequate performance for the analytes of interest. The use of other SPE configurations will require modifications to the procedures described in Sec. 7.0. Consult the manufacturer's instruction**s** regarding such modifications.

4.1 Solid-phase disk extraction system - Empore™ manifold that holds three 90-mm filter standard apparatus or six 47-mm standard filter apparatus, or equivalent. Other manual, automatic, or robotic sample preparation systems designed for solid-phase media may be utilized for this method if adequate performance is achieved and all quality control requirements are satisfied.

4.1.1 Manifold station - (Fisher Scientific 14-378-1B [3-place], 14-378-1A [6-place], or equivalent).

4.1.2 Standard filter apparatus - (Fisher Scientific 14-378-2A [47-mm], 14-378-2B [90-mm], or equivalent), consisting of a sample reservoir, clamp, fritted disk and filtration head with drip tip.

4.1.3 Collection tube - 60-mL. The collection tube should be of appropriate ID and length so that the drip tip of the standard filter apparatus can be positioned well into the neck of the tube to prevent splattering.

4.1.4 Filter flask - 2-L with a ground-glass receiver joint (optional). May be used to carry out individual disk extractions with the standard filter apparatus and collection vial in an all-glass system.

4.2 Solid-phase cartridge extraction system - Visiprep solid-phase extraction manifold (Supelco) or equivalent system suitable for use with the extraction cartridges (see Sec. 4.4). Consult the manufacturer’s recommendations for the associated glassware and hardware necessary to perform sample extractions.

4.3 Solid-phase extraction disks - Empore™, 47-mm, 90-mm, or equivalent. Disks are available in 47-mm and 90-mm diameters, composed of a variety of solid-phase materials. Other solid phases may be employed, provided that adequate performance is demonstrated for the analytes of interest. Guidance for selecting the specific disk is provided in Table 1.

4.3.1 C_{18} disks - Empore™ disks, 47-mm diameter (3M product number 98-0503-0015-5), 90-mm diameter (3M product number 98-0503-0019-7), or equivalent.

4.3.2 C_{18} fast flow disks - Empore™ disks, 47-mm diameter (3M product number 98-0503-0138-5), 90-mm diameter (3M product number 98-0503-0136-9), or equivalent. These disks may be a better choice for samples that are difficult to filter even with the use of a filter aid.

4.3.3 Styrene divinylbenzene (SDB-XC) disks - Empore™ disks, 47-mm diameter (3M product number 98-0503-0067-6), 90-mm diameter (3M product number 98-0503-0068-4), or equivalent.

4.3.4 Styrene divinylbenzene reversed-phase sulfonated (SDB-RPS) disks - Empore™ disks, 47-mm diameter (3M product number 98-0503-0110-4), 90-mm diameter (3M product number 98-0503-0111-2), or equivalent.

4.4 Solid-phase extraction cartridges - Porapak® R SPE device, Waters Corporation, or equivalent. Other solid phases may be employed, provided that adequate performance is demonstrated for the analytes of interest.

4.5 Filtration aid (optional)

4.5.1 Filter Aid 400 - (Fisher Scientific 14-378-3, or equivalent).

4.5.2 In-situ glass micro-fiber prefilter - (Whatman GMF 150, 1-μm pore size, or equivalent).

4.6 Drying column - 22-mm ID glass chromatographic column with a PTFE stopcock (Kontes K-420530-0242, or equivalent).

NOTE: *Fritted glass discs used to retain sodium sulfate in some columns are difficult to decontaminate after contact with highly contaminated or viscous extracts. Columns suitable for this method use a small pad of glass wool to retain the drying agent.*

4.7 Kuderna-Danish (K-D) apparatus

4.7.1 Concentrator tube - 10-mL, graduated. A ground-glass stopper is used to prevent evaporation of extracts during short-term storage.

4.7.2 Evaporation flask - 500-mL, or other size appropriate for the volumes of solvents to be concentrated. Attach to concentrator tube using springs or clamps.

4.7.3 Three-ball macro-Snyder column.

4.7.4 Two-ball micro-Snyder column (optional).

4.7.5 Springs - ½-inch.

4.8 Solvent Vapor Recovery System - Kontes 545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent.

NOTE: *The glassware in Sec. 4.6 is recommended for the purpose of solvent recovery during the concentration procedures (Secs. 7.10 and 7.11) requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.*

4.9 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide, or equivalent).

4.10 Water bath - Heated, with concentric ring cover, capable of temperature control to within ± 5°C. The bath should be used in a hood.

4.11 Nitrogen evaporation apparatus (optional) - N-Evap, 12- or 24-position (Organomation Model 112, or equivalent).

4.12 Vials, glass - Sizes as appropriate, e.g., 2-mL or 10-mL, with PTFE-lined screw caps or crimp tops for storage of extracts.

4.13 pH indicator paper - Wide pH range.

4.14 Vacuum system - Capable of maintaining a vacuum of approximately 66 cm (26 inches) of mercury.

4.15 Graduated cylinders - Sizes as appropriate.

4.16 Pipets - disposable.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without decreasing the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 - Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride.

5.4 Solutions for adjusting the pH of samples before extraction.

5.4.1 Sulfuric acid solution (1:1 v/v), H_2SO_4 - Slowly add 50 mL of concentrated H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.4.2 Sodium hydroxide solution (10N), NaOH - Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.5 Extraction, washing, and exchange solvents - At a minimum, all solvents must be pesticide quality or equivalent.

5.5.1 Methylene chloride, CH_2Cl_2.

5.5.2 Hexane, C_6H_{14}.

5.5.3 Ethyl acetate, $CH_3C(OH)OCH_2CH_3$.

5.5.4 Acetonitrile, CH_3CN.

5.5.5 Methanol, CH_3OH.

5.5.6 Acetone, $(CH_3)_2CO$.

5.5.7 Methyl-*tert*-butyl ether (MTBE), $C_5H_{12}O$.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to Chapter Four, Organic Analytes, Sec. 4.1, Method 3500, Sec. 7.1 of this method, and the specific determinative methods to be employed.

7.0 PROCEDURE

The procedures for solid-phase extraction are very similar for most organic analytes. Therefore, this section describes procedures for sample preparation, pH adjustment, preparation of the extraction apparatus, and extract concentration that apply to all target analytes. The

procedures for disk washing, disk conditioning, sample extraction, and sample elution vary among the groups of analytes.

7.1 Sample preparation

Most of the specific procedures described in this method were developed for a nominal sample size of 1 L, as this sample size is usually employed for other extraction methods such as separatory funnel or continuous liquid-liquid extraction. This method also may be employed with smaller samples when overall analytical sensitivity is not a concern or when high levels of the target analytes are anticipated. However, such samples are best collected in a container of appropriate size. The extraction of aqueous samples presents several challenges that must be considered during sample preparation. First, the analytes of interest are often associated with the particulate matter in the sample and sample preparation procedures must ensure that any particulates in the original sample are included in the sample aliquot that is extracted. Secondly, the majority of the organic analytes are hydrophobic and may preferentially adhere to the surfaces of the sample container. For this reason, most extraction methods have traditionally specified that once the sample has been transferred to the extraction apparatus, the sample container be rinsed with solvent which is added to the apparatus. As a result, it is generally not appropriate to extract only part of the sample from a sample container, e.g., 250 mL from a 1-L sample bottle.

The appropriate sample volume may vary with the intended use of the results and, in general, is the volume necessary to provide the analytical sensitivity necessary to meet the objectives of the project (see Chapter Two). Under ideal conditions, the sample should be collected by completely filling the container. The sample should generally be collected without additional volume and with little or no headspace. Thus, a 1-L sample is collected in a 1-L container, a 250-mL sample is collected in a 250-mL container, etc.

Any surrogates and matrix spiking compounds (if applicable) are added to the sample in the original container. The container is then recapped and shaken to mix the spiked analytes into the sample. The extraction of some groups of analytes also requires that the pH of the sample be adjusted to a specified value (see Table 1). When pH adjustment is necessary, it should be performed after the surrogates and matrix spiking compounds (if applicable) have been added and mixed with the sample. Otherwise, the recoveries of these compounds will have little relevance to those of the target analytes in the sample.

If this approach is not possible, then a sample aliquot may be transferred to a graduated cylinder and spiked. However, in such instances, the analyst must take great care to mix the sample well, by shaking, to ensure a homogeneous distribution of the particulate matter and must record the fact that the container was not rinsed.

NOTE: *This method may not be appropriate for aqueous samples with greater than 1% solids, as such samples can be difficult to filter and the extraction efficiency may be reduced as a result of the small volumes of solvents employed and the short contact time. If the particulate load significantly slows or prevents filtration, it may be more appropriate to employ an alternative extraction procedure.*

7.1.1 Mark the level of the sample on the outside of the sample container for later determination of the sample volume used. Shake the container for several minutes, with the cap tightly sealed, to ensure that any particulate matter is evenly distributed throughout the sample.

7.1.2 Prepare a method blank from a 1-L volume of organic-free reagent water, or a volume similar to that of the samples (e.g., a 250-mL blank should be used when the sample size is 250 mL, etc.). The blank may be prepared in a graduated cylinder, beaker, or other suitable container. The frequency of method blank preparation is described in Chapter One.

7.1.3 Add any surrogate standards listed in the determinative method to the samples in their original containers and to the blank. For disk extractions, also add 5.0 mL of methanol to each sample in the original container. All samples, blanks, and QC samples should receive the same amount of methanol. (This step is not necessary for the cartridge extraction of nitroaromatics and nitramines.) Shake the samples to mix the surrogates and allow the sample to stand for at least several minutes. This will permit the surrogates to dissolve in the sample and will also allow the particulate matter to settle after spiking, which will speed the filtration process somewhat.

7.1.4 Prepare matrix spikes by adding listed matrix spike standards to representative sample replicates in their original containers . The frequency with which matrix spikes are prepared and analyzed is described in Chapter One or as part of the determinative method. Mix the matrix spike samples as described in Sec.7.1.3 and allow to stand.

7.1.5 If cleanup procedures are to be employed that result in the loss of extract, adjust the amount of surrogate and spiking cocktail(s) accordingly. In the case of Method 3640, Gel Permeation Cleanup, double the amount of standards to compensate for the loss of one half of the extract concentrate when loading the GPC column.

7.2 pH adjustment

Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to the range listed below. If pH adjustment is required, this step should be performed in the original sample container to ensure that analytes are not lost in precipitates or flocculated material. Any adjustment of the sample pH should take place after the surrogates and matrix spiking compounds are added, so that they are affected by the pH in the same manner as the target analytes.

NOTE: *The efficiency of solid-phase extraction of acid herbicide compounds is greatly affected by pH. If acid herbicides are to be extracted from TCLP leachates or other samples, adjust the pH to 1.0 before extraction.*

Analyte Group	Extraction pH
Phthalate esters	5 - 7
Organochlorine pesticides	5 - 9
Polychlorinated biphenyls (PCBs)	5 - 9
Organophosphorus pesticides	as received
Nitroaromatics and nitramines	as received
TCLP leachates containing organochlorine pesticides	as produced by TCLP
TCLP leachates containing semivolatiles	as produced by TCLP
TCLP leachates containing phenoxyacid herbicides	1.0

7.3 Setting up the extraction apparatus

7.3.1 Assemble a manifold for multiple disk extractions (Figure 1) using 47-mm or 90-mm extraction disks. Use a filter flask with the standard filter apparatus for single extractions. The solid-phase disks that are generally appropriate for each group of analytes are listed below, and in Table 1.

Analyte Group	Disk Medium
Phthalate esters	C_{18}
Organochlorine pesticides	C_{18}
Polychlorinated biphenyls (PCBs)	C_{18}
Organophosphorus pesticides	SDB-RPS
Nitroaromatics and nitramines	SDB-RPS
TCLP leachates containing organochlorine pesticides	SDB-XC
TCLP leachates containing semivolatiles	SDB-XC
TCLP leachates containing phenoxyacid herbicides	SDB-XC

For nitroaromatics and nitramines, samples also may be extracted using an SPE cartridge. Assemble the cartridge apparatus according to the manufacturer's instructions, using Porapak R, or equivalent, SPE cartridges, and proceed to Sec. 7.6.

7.3.2 If samples contain significant quantities of particulates, the use of a filter aid or prefilter is advisable for disk extractions. Empore™ Filter Aid 400, Whatman GMF 150, or equivalent prefilters are recommended.

7.3.2.1 Pour about 40 g of Filter Aid 400 onto the surface of the disk after assembling the standard filter apparatus.

7.3.2.2 Alternatively, place the Whatman GMF 150 on top of the extraction disk prior to clamping the glass reservoir into the standard filter apparatus.

7.3.2.3 Do not add the filter aid if using the cartridge extraction procedure for nitroaromatics and nitramines.

7.4 Washing the extraction apparatus

Prior to use, the extraction disks must undergo two separate washing steps, usually with different solvents. The steps involved in washing the extraction apparatus before use depend on the analytes of interest and the sample matrix.

7.4.1 First washing step

The following table illustrates the solvents recommended for the first washing step.

Analyte Group	1st solvent wash volume
Phthalate esters	20 mL methylene chloride
Organochlorine pesticides	20 mL methylene chloride
Polychlorinated biphenyls (PCBs)	20 mL methylene chloride
Organophosphorus pesticides	5 mL acetone
Nitroaromatics and nitramines	5 mL acetonitrile
TCLP leachates containing organochlorine pesticides	5 mL acetone
TCLP leachates containing semivolatiles	5 mL acetone
TCLP leachates containing phenoxyacid herbicides	5 mL acetonitrile

Wash the extraction apparatus and disk with the volume of the solvent listed above by rinsing the solvent down the sides of the glass reservoir. Pull a small amount of solvent through the disk with a vacuum. Turn off the vacuum and allow the disk to soak for about one minute. Pull the remaining solvent through the disk and allow the disk to dry.

7.4.1.1 When using a filtration aid, adjust the volume of all wash solvents so the entire filtration bed is submerged.

7.4.1.2 In subsequent conditioning steps, volumes should be adjusted so that a level of solvent is always maintained above the entire filter bed.

7.4.2 Second washing step

The following table illustrates the solvents recommended for the second washing step.

Analyte Group	2nd solvent wash volume
Phthalate esters	10 mL acetone
Organochlorine pesticides	10 mL acetone
Polychlorinated biphenyls (PCBs)	not required
Organophosphorus pesticides	5 mL methanol
Nitroaromatics and nitramines	15 mL acetonitrile
TCLP leachates containing organochlorine pesticides	5 mL ethyl acetate
TCLP leachates containing semivolatiles	5 mL ethyl acetate
TCLP leachates containing phenoxyacid herbicides	not required

7.5 Disk conditioning

The extraction disks are composed of hydrophobic materials which will not allow water to pass unless they are pre-wetted with a water-miscible solvent before being used for sample extraction. This step is referred to as conditioning, and the solvent used is dependent on the analytes of interest. The following table illustrates the solvents recommended for specific groups of analytes.

NOTE: *Beginning with the conditioning step, it is CRITICAL that the disk NOT go dry until after the extraction steps are completed. Should a disk accidentally go dry during the conditioning steps, the conditioning steps for that disk must be repeated prior to adding the sample.*

Analyte Group	Conditioning steps
Phthalate esters	20 mL methanol, soak 1 min, 20 mL reagent water
Organochlorine pesticides	20 mL methanol, soak 1 min, 20 mL reagent water
Polychlorinated biphenyls (PCBs)	20 mL methanol, soak 1 min, 20 mL reagent water
Organophosphorus pesticides	5 mL methanol, soak 1 min, 20 mL reagent water
Nitroaromatics and nitramines	15 mL acetonitrile, soak 3 min 30 mL reagent water
TCLP leachates containing organochlorine pesticides	5 mL methanol soak 1 min, 15 mL reagent water
TCLP leachates containing semivolatiles	5 mL methanol soak 1 min, 15 mL reagent water
TCLP leachates containing phenoxyacid herbicides	5 mL methanol soak 1 min, 15 mL reagent water

7.5.1 Add the conditioning solvent to the extraction apparatus. Apply a vacuum until a few drops of solvent pass through the disk, ensuring that the disk is soaked with the solvent. Turn off the vacuum and allow the disk to soak in the solvent for the time specified above.

7.5.2 When using a filtration aid, adjust the volume of conditioning solvents so that the entire filtration bed remains submerged until the extraction is completed.

7.5.3 Once the soaking time is over, apply the vacuum again, drawing all but a thin layer of solvent through the disk. Stop the vacuum just before the disk goes dry.

7.5.4 Add the volume of organic-free reagent water listed above and apply vacuum to draw the water through the disk. Stop the vacuum just before the disk goes dry, leaving 2-3 mm of water above the surface of the disk.

7.5.5 Proceed to Sec. 7.7 for the sample extraction instructions.

7.6 Cartridge procedure for nitroaromatics and nitramines

Aqueous samples to be analyzed for nitroaromatics and nitramines may also be extracted using the SPE cartridge technique described below. The same sample preparation considerations discussed in Sec. 7.1 also apply to this procedure.

7.6.1 After assembling the SPE cartridge in the extraction apparatus (see Sec. 7.3.1), wash the cartridge with 10 mL of acetonitrile, using gravity flow. Do not allow the cartridge to go dry.

7.6.2 When only a thin layer of solvent remains above the sorbent bed in the cartridge, add 30 mL of reagent water to the cartridge and allow it to flow through the sorbent bed under gravity flow. Stop the flow just before the cartridge goes dry.

7.6.3 Attach a connector to the top of the cartridge. The other end of the connector should be fitted with flexible PTFE tubing long enough to reach into the sample bottle or other container (e.g., a beaker) holding the sample.

7.6.4 Turn on the vacuum, and draw the sample through the cartridge at a rate of about 10 mL/min, until all of the sample has passed through the cartridge. As particulate matter plugs the cartridge and slows the flow, increase the vacuum to maintain a reasonable flow rate.

7.6.5 Once all of the sample has been pulled through the cartridge, shut off the vacuum and add 5 mL of reagent water to the cartridge. Allow the reagent water to pass through the cartridge under gravity flow, if practical, or apply a vacuum to complete the process. Shut off the flow once the water has been drawn through the cartridge.

7.6.6 Method blanks and matrix spike aliquots (Sec. 7.1) are handled in the same manner as the samples.

7.6.7 Proceed with sample elution, as described in Sec. 7.9.

7.7 Sample extraction using SPE disks

7.7.1 Pour the sample into the reservoir and, under full vacuum, filter it as quickly as the vacuum will allow (at least 10 minutes). Transfer as much of the measured volume of water as possible.

NOTE: With heavily particle-laden samples, allow the sediment in the sample to settle and decant as much liquid as is practical into the reservoir. After most of the aqueous portion of the sample has passed through the disk, swirl the portion of the sample containing sediment and add it to the reservoir. Use additional portions of organic-free reagent water to transfer any remaining particulates to the reservoir. Particulates must be transferred to the reservoir before all of the aqueous sample has passed through the disk.

7.7.2 After the sample has passed through the solid-phase media, dry the disk by maintaining vacuum for about 3 minutes. Method blanks and matrix spike aliquots (Sec. 7.1) are handled in the same manner as the samples.

7.8 Elution of the analytes from the disk

The choice of elution solvent is critical to the success of solid-phase extraction. The recommended elution solvent for each group of analytes is listed below.

Analyte Group	Sample elution steps
Phthalate esters	5 mL acetone, soak 15-20 sec. Rinse bottle with 15 mL acetonitrile and add to disk.
Organochlorine pesticides	5 mL acetone, soak 15-20 sec. Rinse bottle with 15 mL methylene chloride and add to disk.
Polychlorinated biphenyls (PCBs)	5 mL acetone, soak 15-20 sec. Rinse bottle with 20 mL acetonitrile and add to disk.
Organophosphorus pesticides	0.6 mL acetone, soak 1 min. Rinse bottle with 5 mL MTBE and add to disk. Repeat bottle rinse twice more.
Nitroaromatics and nitramines	5 mL acetonitrile, soak 3 min.
TCLP leachates containing organochlorine pesticides	Rinse bottle with 4 mL acetone and add to disk. Rinse glassware with 2 mL acetone and add to disk. Soak 1 min. Rinse bottle twice with 5 mL ethyl acetate and add to disk.

TCLP leachates containing semivolatiles	Rinse bottle with 4 mL acetone and add to disk. Rinse glassware with 2 mL acetone and add to disk. Soak 1 min. Rinse bottle twice with 5 mL ethyl acetate and add to disk.
TCLP leachates containing phenoxyacid herbicides	Rinse bottle with 5 mL acetonitrile and add to disk. Soak 1 min. Rinse bottle twice more with 5 mL acetonitrile and add to disk.

7.8.1 Remove the entire standard filter assembly (do not disassemble) from the manifold and insert a collection tube. The collection tube should have sufficient capacity to hold all of the elution solvents. The drip tip of the filtration apparatus should be seated sufficiently below the neck of the collection tube to prevent analyte loss due to splattering when vacuum is applied. When using a filter flask for single extractions, empty the water from the flask before inserting the collection tube.

7.8.2 An initial elution with a water-miscible solvent, i.e., acetone or acetonitrile, improves the recovery of analytes trapped in water-filled pores of the sorbent. Use of a water-miscible solvent is particularly critical when methylene chloride is used as the second elution solvent. With the collection tube in place, add the volume of elution solvent listed above to the extraction apparatus. Allow the solvent to spread out evenly across the disk (or inert filter) then quickly turn the vacuum on and off to pull the first drops of sovlent through the disk. Allow the disk to soak for 15 to 20 seconds before proceeding to Sec. 7.8.3

7.8.3 Rinse the sample bottle and/or glassware that held the sample with the second solvent listed above and transfer the solvent rinse to the extraction apparatus. As needed, use a disposable pipette to rinse the sides of the extraction apparatus with solvent from the bottle.

7.8.4 Draw about half of the solvent through the disk and then release the vacuum. Allow the remaining elution solvent to soak the disk and particulates for about one minute before drawing the remaining solvent through the disk under vacuum. When using a filtration aid, adjust the volume of elution solvent so that the entire filtration bed is initially submerged.

7.8.5 Repeat the bottle rinsing step as listed in the table above, continuing to apply vacuum and collecting the solvent in the tube.

7.9 Eluting the nitroaromatics and nitramines from the cartridge

Once the reagent water has passed through the column, place a collection tube under the cartridge. Add 5 mL of acetonitrile to the top of the cartridge and allow it to pass through the cartridge under gravity flow, collecting the solvent in the collection tube. Measure the volume of acetonitrile recovered from the cartridge.

7.10 K-D concentration technique

Where necessary to meet the sensitivity requirements, sample extracts may be concentrated to the final volume necessary for the determinative method and specific application, using the K-D technique or nitrogen evaporation.

7.10.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to an appropriately sized evaporation flask.

7.10.2 Dry the combined extracts in the collection tube (Secs. 7.8 and 7.9) by passing them through a drying column containing about 10 g of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Use acidified sodium sulfate (see Method 8151) if acidic analytes are to be measured.

7.10.3 Rinse the collection tube and drying column into the K-D flask with an additional 20-mL portion of solvent in order to achieve a quantitative transfer.

7.10.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Attach the solvent vapor recovery glassware (condenser and collection device, see Sec. 4.6) to the Snyder column of the K-D apparatus, following the manufacturer's instructions. Pre-wet the Snyder column by adding about 1 mL of methylene chloride (or other suitable solvent) to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.10.4.1 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip.

7.10.4.2 Reattach the Snyder column. Concentrate the extract, raising the temperature of the water bath, if necessary, to maintain a proper distillation rate.

7.10.5 Remove the Snyder column. Rinse the K-D flask and the lower joints of the Snyder column into the concentrator tube with 1 - 2 mL of solvent. The extract may be further concentrated by using one of the techniques outlined in Sec. 7.11, or adjusted to a final volume of 5.0 - 10.0 mL using an appropriate solvent (Table 1).

7.11 If further concentration is required, use either the micro-Snyder column technique (7.11.1) or nitrogen evaporation technique (7.11.2).

7.11.1 Micro-Snyder column technique

7.11.1.1 Add a fresh clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column directly to the concentrator tube. Attach the solvent vapor recovery glassware (condenser and collection device) to the micro-Snyder column of the K-D apparatus, following the manufacturer's instructions. Pre-wet the Snyder column by adding 0.5 mL of methylene chloride or the exchange solvent to the top of the column. Place the micro-concentration apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as necessary, to complete the concentration in 5 - 10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

7.11.1.2 When the apparent volume of liquid reaches 0.5 mL, remove the apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final extract volume to 1.0 - 2.0 mL.

7.11.2 Nitrogen evaporation technique

7.11.2.1 Place the concentrator tube in a warm bath (30°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce phthalate interferences.

7.11.2.2 Rinse down the internal wall of the concentrator tube several times with solvent during the concentration. During evaporation, position the concentrator tube to avoid condensing water into the extract. Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, some semivolatile analytes such as cresols may be lost.

7.12 The extract may now be subjected to cleanup procedures or analyzed for the target analytes using the appropriate determinative technique(s). If further handling of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a PTFE-lined screw-cap, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used for actual samples.

8.2 Refer to Chapter One for general quality control procedures and Method 3500 for specific QC procedures for extraction and sample preparation.

9.0 METHOD PERFORMANCE

Refer to the determinative methods listed in Sec. 1.1 for performance data related to solid-phase extraction.

10.0 REFERENCES

1. Lopez-Avila, V., Beckert, W., et. al., "Single Laboratory Evaluation of Method 8060 - Phthalate Esters", EPA/600/4-89/039.

2. Tomkins, B.A., Merriweather, R., et. al., "Determination of Eight Organochlorine Pesticides at Low Nanogram/Liter Concentrations in Groundwater Using Filter Disk Extraction and Gas Chromatography", JAOAC International, 75(6), pp. 1091-1099 (1992).

3. Markell, C., "3M Data Submission to EPA," letter to B. Lesnik, June 27, 1995.

4. Jenkins, T. F., Thorne, P. G., Myers, K. F., McCormick, E. F., Parker, D. E., and B. L. Escalon (1995). Evaluation of Clean Solid Phases for Extraction of Nitroaromatics and Nitramines from Water. USACE Cold Regions Research and Engineering Laboratory, Special Report 95-22.

TABLE 1

SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative Method	Extraction pH	Disk Medium[a]	Elution Solvent	Exchange Solvent	Final Extract Volume for Analysis (mL)[b]
8061 (phthalate esters)	5-7	C_{18}	acetonitrile	hexane	10.0
8081 (organochlorine pesticides)	5-9	C_{18}	methylene chloride	hexane	10.0
8082 (PCBs)	5-9	C_{18}	methylene chloride	hexane	10.0
8141 (organophosphorus pesticides)	as received	SDB-RPS	MTBE	hexane	10.0
8330 (nitroaromatics and	as received	SDB-RPS	acetonitrile	acetonitrile	10.0

nitramines)					
TCLP pesticides (8081)	as produced by TCLP	SDB-XC	ethyl acetate	hexane	10.0
TCLP semivolatiles (8270)	as produced by TCLP	SDB-XC	ethyl acetate	methylene chloride	1.0
TCLP phenoxyacid herbicides (8321)	1.0	SDB-XC	acetonitrile	hexane	10.0

[a] SDB has a greater capacity than C_{18} and a greater affinity for more analytes but they may be more difficult to elute.

[b] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

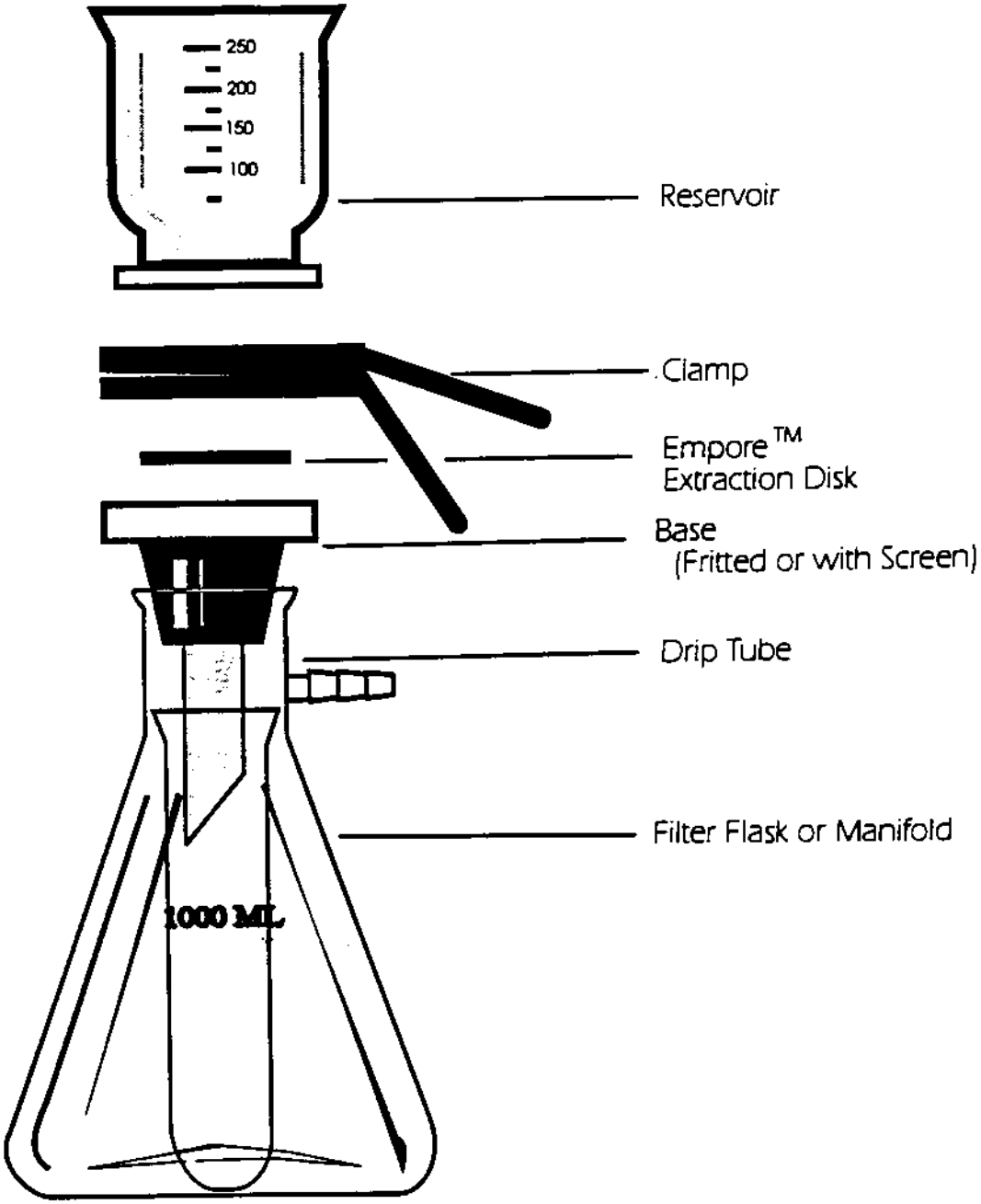
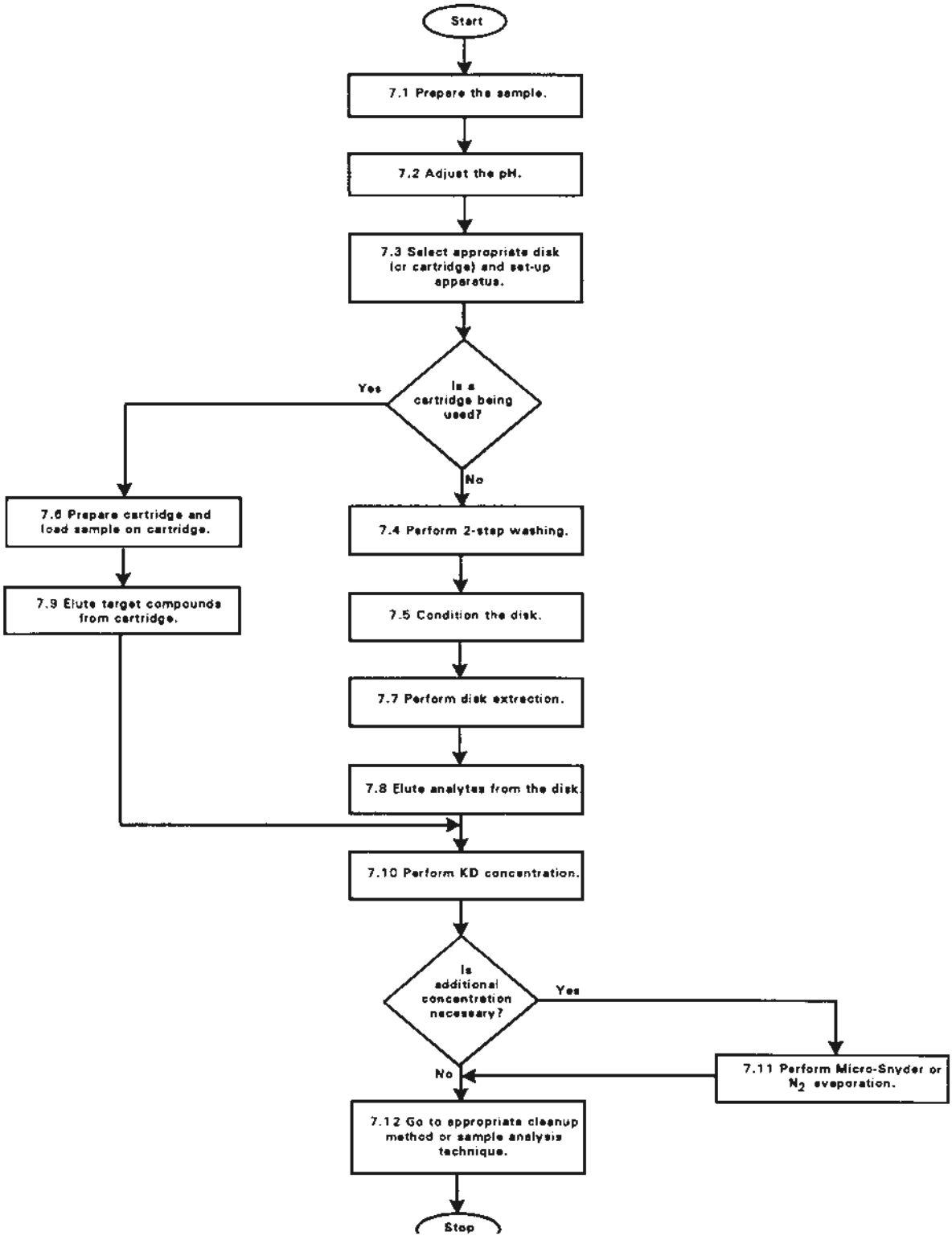

250
200
150
100
Reservoir
Clamp
Empore™
Extraction Disk
Base
(Fritted or with Screen)
Drip Tube
Filter Flask or Manifold
1000 ML

FIGURE 1

DISK EXTRACTION APPARATUS

METHOD 3535A

SOLID-PHASE EXTRACTION (SPE)


Start
7.1 Prepare the sample.
7.2 Adjust the pH.
7.3 Select appropriate disk (or cartridge) and set-up apparatus.
Is a cartridge being used?
Yes
No
7.6 Prepare cartridge and load sample on cartridge.
7.9 Elute target compounds from cartridge.
7.4 Perform 2-step washing.
7.5 Condition the disk.
7.7 Perform disk extraction.
7.8 Elute analytes from the disk.
7.10 Perform KD concentration.
Is additional concentration necessary?
Yes
No
7.11 Perform Micro-Snyder or N_2 evaporation.
7.12 Go to appropriate cleanup method or sample analysis technique.
Stop

METHOD 3540C

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor.

2.2 The extract is then dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 40 mm ID, with 500-mL round bottom flask.

4.2 Drying column - 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.4 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.5 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Vials - Glass, 2-mL capacity, with polytetrafluoroethylene (PTFE)-lined screw or crimp top.

4.8 Glass or paper thimble or glass wool - Contaminant-free.

4.9 Heating mantle - Rheostat controlled.

4.10 Disposable glass pasteur pipet and bulb.

4.11 Apparatus for determining percent dry weight.

4.11.1 Drying oven - capable of maintaining 105°C.

4.11.2 Desiccator.

4.11.3 Crucibles - Porcelain or disposable aluminum.

4.12 Apparatus for grinding

4.13 Analytical balance - capable of weighing to 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents - All solvents must be pesticide quality or equivalent.

5.4.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems:

5.4.1.1 Acetone/Hexane (1:1) (v/v), CH_3COCH_3/C_6H_{14}.

NOTE: This solvent system has lower disposal cost and lower toxicity.

5.4.1.2 Methylene chloride/Acetone (1:1 v/v), CH_2Cl_2/CH_3COCH_3.

5.4.2 Other samples shall be extracted using the following:

5.4.2.1 Methylene chloride, CH_2Cl_2.

5.4.2.2 Toluene/Methanol (10:1) (v/v), $C_6H_5CH_3/CH_3OH$.

5.5 Exchange solvents - All solvents must be pesticide quality or equivalent.

5.5.1 Hexane, C_6H_{14}.

5.5.2 2-Propanol, $(CH_3)_2CHOH$.

5.5.3 Cyclohexane, C_6H_{12}.

5.5.4 Acetonitrile, CH_3CN.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample Handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiple phases must be prepared by the phase separation method in Chapter Two before extraction. This extraction procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.1.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of anhydrous sodium sulfate to the sample (1:1) may make the mixture amenable to grinding.

7.2 Determination of percent dry weight - When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or be vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

Immediately after weighing the sample for extraction, weigh 5 - 10 g of the sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\%\ \text{dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

This oven-dried aliquot is not used for the extraction and should be disposed of appropriately once the dry weight has been determined.

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble.

7.3.1 Add 1.0 mL of the surrogate standard spiking solution onto the sample (see Method 3500 for details on the surrogate standard and matrix spiking solutions).

7.3.2 For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard.

7.3.3 Consult Secs. 5.5 and 8.3 of Method 3500 for the appropriate choice of matrix spiking compounds and concentrations.

7.4 Place approximately 300 mL of the extraction solvent (Sec. 5.4) into a 500-mL round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16 - 24 hours at 4 - 6 cycles/hour.

7.5 Allow the extract to cool after the extraction is complete.

7.6 Assemble a Kuderna-Danish (K-D) concentrator (Sec. 4.3), if necessary, by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.7 Attach the solvent vapor recovery glassware (condenser and collection device) (Sec. 4.4) to the Snyder column of the K-D apparatus following manufacturer's instructions.

7.8 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer.

7.9 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15 - 20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 - 20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 - 2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.10 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add approximately 50 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Sec. 7.9, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1 - 2 mL, remove the K-D apparatus from the water batch and allow it to drain and cool for at least 10 minutes.

7.11 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the techniques described in Sec. 7.12 or adjusted to 10.0 mL with the solvent last used.

7.12 If further concentration is indicated in Table 1, either micro Snyder column technique (Sec. 7.12.1) or nitrogen blowdown technique (Sec. 7.12.2) is used to adjust the extract to the final volume required.

7.12.1 Micro Snyder column technique

7.12.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding about 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5 - 10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.

7.12.1.2 When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the concentrator tube. Adjust the final volume to 1.0 - 2.0 mL, as indicated in Table 1, with solvent.

7.12.2 Nitrogen blowdown technique

7.12.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample, since it may introduce contaminants.

7.12.2.2 The internal wall of the tube must be rinsed several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.13 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and refrigerate. If the extract will be stored longer than 2 days, it should be transferred to a vial with a PTFE-lined screw cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

None.

TABLE 1

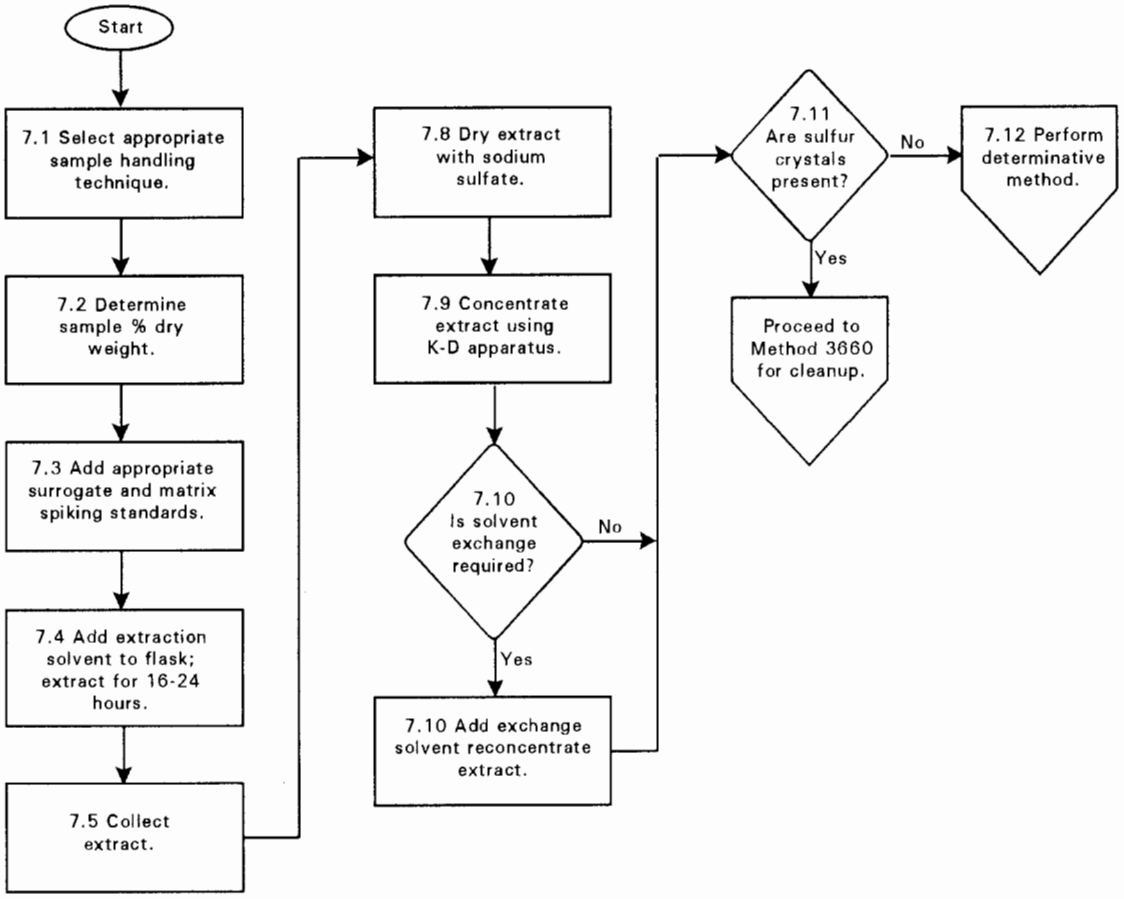
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent for analysis	Exchange solvent for cleanup	Volume of extract for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	as received	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8082	as received	hexane	hexane	10.0	10.0
8091	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8111	as received	hexane	hexane	2.0	10.0
8121	as received	hexane	hexane	2.0	1.0
8141	as received	hexane	hexane	10.0	10.0
8270[c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0
8321	as received	methanol	-	-	1.0
8325	as received	methanol	-	-	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

[b] Phenols may be analyzed by Method 8041, using a 1.0-mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5-mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.


Start
7.1 Select appropriate sample handling technique.
7.2 Determine sample % dry weight.
7.3 Add appropriate surrogate and matrix spiking standards.
7.4 Add extraction solvent to flask; extract for 16-24 hours.
7.5 Collect extract.
7.8 Dry extract with sodium sulfate.
7.9 Concentrate extract using K-D apparatus.
7.10 Is solvent exchange required?
No
Yes
7.10 Add exchange solvent reconcentrate extract.
7.11 Are sulfur crystals present?
No
Yes
7.12 Perform determinative method.
Proceed to Method 3660 for cleanup.

METHOD 3541

AUTOMATED SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3541 describes the extraction of organic analytes from soil, sediment, sludges, and waste solids. The method uses a commercially available, unique, three stage extraction system to achieve analyte recovery comparable to Method 3540, but in a much shorter time. There are two differences between this extraction method and Method 3540. In the initial extraction stage of Method 3541, the sample-loaded extraction thimble is immersed into the boiling solvent. This ensures very rapid intimate contact between the specimen and solvent and rapid extraction of the organic analytes. In the second stage the thimble is elevated above the solvent, and is rinse-extracted as in Method 3540. In the third stage, the solvent is evaporated, as would occur in the Kuderna-Danish (K-D) concentration step in Method 3540. The concentrated extract is then ready for cleanup (Method 3600) followed by measurement of the organic analytes.

1.2 The method is applicable to the extraction and concentration of water insoluble or slightly water soluble polychlorinated biphenyls (PCBs) in preparation for gas chromatographic determination using either Method 8080 or 8081. This method is applicable to soils, clays, solid wastes and sediments containing from 1 to 50 µg of PCBs (measured as Arochlors) per gram of sample. It has been statistically evaluated at 5 and 50 µg/g of Arochlors 1254 and 1260, and found to be equivalent to Method 3540 (Soxhlet Extraction). Higher concentrations of PCBs are measured following volumetric dilution with hexane.

1.3 The method is also applicable the extraction and concentration of semivolatile organics in preparation for GC/MS analysis by Method 8270 or by analysis using specific GC or HPLC methods.

2.0 SUMMARY OF METHOD

2.1 PCBs: Moist solid samples (e.g., soil/sediment samples) may be air-dried and ground prior to extraction or chemically dried with anhydrous sodium sulfate. The prepared sample is extracted using 1:1 (v/v) acetone:hexane in the automated Soxhlet following the same procedure as outlined for semivolatile organics in Sec. 2.1. The extract is then concentrated and exchanged into pure hexane prior to final gas chromatographic PCB measurement.

2.2 Other semivolatile organics: A 10-g solid sample (the sample is pre-mixed with anhydrous sodium sulfate for certain matrices) is placed in an extraction thimble and usually extracted with 50 mL of 1:1 (v/v) acetone/hexane for 60 minutes in the boiling extraction solvent. The thimble with sample is then raised into the rinse position and extracted for an additional 60 minutes. Following the extraction steps, the extraction solvent is concentrated to 1 to 2 mL.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The extraction thimble and the o-rings used to seal the extraction cup are both a source of interference. Both should be checked by including a method blank and following the extraction procedure as written. Solvent rinsing or extraction, prior to use, may be necessary to eliminate or reduce interferences. Viton seals contributed least to the interference problem, however, even they contributed some interference peaks when the extraction solvent was analyzed by the electron capture detector. Use of butyl or EPDM rings are not recommended since they were found to contribute significant background when the extraction solvent was 1:1 v/v hexane/acetone or 1:1 v/v methylene chloride/acetone.

4.0 APPARATUS AND MATERIALS

4.1 Automated Soxhlet Extraction System - with temperature-controlled oil bath (Soxtec, or equivalent). Tecator bath oil (catalog number 1000-1886) should be used with the Soxtec. Silicone oil must not be used because it destroys the rubber parts. See Figure 1. The apparatus is used in a hood.

4.2 Accessories and consumables for the automated Soxhlet system. (The catalog numbers are Fisher Scientific based on the use of the Soxtec HT-6, however, other sources that are equivalent are acceptable.)

4.2.1 Cellulose extraction thimbles - 26 mm ID x 60 mm contamination free, catalog number 1522-0034, or equivalent.

4.2.2 Glass extraction cups (80 mL) - (set of six required for the HT-6), catalog number 1000-1820.

4.2.3 Thimble adapters - (set of six required for the HT-6), catalog number 1000-1466.

4.2.4 Viton seals - catalog number 1000-2516.

4.3 Syringes - 100 and 1000 µL and 5 mL.

4.4 Apparatus for Determining Percent Dry Weight

4.4.1 Drying Oven.

4.4.2 Desiccator.

4.4.3 Crucibles, porcelain.

4.4.4 Balance, analytical.

4.5 Apparatus for grinding - Fisher Cyclotec, Fisher Scientific catalog number 1093, or equivalent.

4.6 Spatula

4.7 Graduated cylinder - 100 mL.

4.8 Aluminum weighing dish - VWR Scientific catalog number 25433-008 or equivalent.

4.9 Graduated, conical-bottom glass tubes - 15 mL, Kimble catalog number 45166 or equivalent, or 10 mL KD concentrator tube.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. A method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents:

5.4.1 Organochlorine pesticides/PCB extraction:

5.4.1.1 Acetone/hexane (1:1 v/v), CH_3COCH_3/C_6H_{14}. Pesticide quality or equivalent.

5.4.2 Semivolatile organics extraction:

5.4.2.1 Acetone/hexane (1:1 v/v), CH_3COCH_3/C_6H_{14}. Pesticide quality or equivalent.

5.4.2.2 Acetone/methylene chloride (1:1 v/v), CH_3COCH_3/CH_2Cl_2. Pesticide quality or equivalent.

5.5 Hexane, C_6H_{14}. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.1.1 PCBs or high-boiling organochlorine pesticides - Air-dry the sample at room temperature for 48 hours in a glass tray or on hexane-cleaned aluminum foil, or dry the sample by mixing with anhydrous sodium sulfate until a free-flowing powder is obtained (see Sec. 7.2).

NOTE: Dry, finely ground soil/sediment allows the best extraction efficiency for non-volatile, non-polar organics, e.g., PCBs, 4,4'-DDT, etc. Air-drying is not appropriate for the analysis of the more volatile organochlorine pesticides (e.g. the BHCs) or the more volatile of the semivolatile organics because of losses during the drying process.

7.1.2 Dried sediment/soil and dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 20 g after grinding. Disassemble grinder between samples, according to manufacturer's instructions, and clean with soap and water, followed by acetone and hexane rinses.

NOTE: The same warning on loss of volatile analytes applies to the grinding process. Grinding should only be performed when analyzing for non-volatile organics.

7.1.3 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. If grinding of these materials is preferred, the addition and mixing of anhydrous sodium sulfate with the sample (1:1) may improve grinding efficiency. The professional judgment of the analyst is required for handling such difficult matrices.

7.1.4 Multiple phase waste samples - Samples consisting of multiple phases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.2 For sediment/soil (especially gummy clay) that is moist and cannot be air-dried because of loss of volatile analytes - Mix 5 g of sample with 5 g of anhydrous sodium sulfate in a small beaker using a spatula. Use this approach for any solid sample that requires dispersion of the sample particles to ensure greater solvent contact throughout the sample mass.

7.3 Determination of sample percent dry weight - In certain cases, sample results are desired based on dry weight basis. When such data are desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from the drying of a heavily contaminated hazardous waste sample.

7.3.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.4 Check the heating oil level in the automated Soxhlet unit and add oil if needed. See service manual for details. Set the temperature on the service unit at 140°C when using hexane-acetone (1:1, v/v) as the extraction solvent.

7.5 Press the "MAINS" button; observe that the switch lamp is now "ON".

7.6 Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/min to prevent solvent loss through the condensers.

7.7 Weigh 10 g of sample into extraction thimbles. For samples mixed with anhydrous sodium sulfate, transfer the entire contents of the beaker (Sec. 7.2) to the thimble. Add surrogate spikes to each sample and the matrix spike/matrix spike duplicate to the selected sample.

NOTE: When surrogate spikes and/or matrix spikes contain relatively volatile compounds (e.g., trichlorobenzenes, BHCs, etc.), steps 7.8, 7.9, and 7.10 must be performed quickly to avoid evaporation losses of these compounds. As the spike is added to the sample in each thimble, the thimble should immediately be transferred to the condenser and lowered into the extraction solvent.

7.8 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

7.9 Insert the extraction cups containing boiling chips, and load each with 50 mL of extraction solvent (normally 1:1 (v/v) hexane:acetone, see Sec. 5.4). Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position. (The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.)

7.10 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.

7.11 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set timer for 60 minutes. Condenser valves are still open. Extract for the preset time.

7.12 After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

7.13 When all but 2 to 5 mL of solvent have been collected, open the system and remove the cups.

7.14 Transfer the contents of the cups to 15 mL graduated, conical-bottom glass tubes. Rinse the cups using hexane (methylene chloride if 1:1 methylene chloride-acetone was used for extraction and analysis is by GC/MS) and add the rinsates to the glass tubes. Concentrate the extracts to 1 to 10 mL. The final volume is dependent on the determinative method and the quantitation limit required. Transfer a portion to a GC vial and store at 4°C until analyses are performed.

NOTE: The recovery solvent volume can be adjusted by adding solvent at the top of the condensers. For more details concerning use of the extractor, see the operating manual for the automated extraction system.

7.15 Shutdown

7.15.1 Turn "OFF" main switch.

7.15.2 Turn "OFF" cold water tap.

7.15.3 Ensure that all condensers are free of solvent. Empty the solvent that is recovered in the evaporation step into an appropriate storage container.

7.16 The extract is now ready for cleanup or analysis, depending on the extent of interfering co-extractives. See Method 3600 for guidance on cleanup methods and Method 8000 for guidance on determinative methods. Certain cleanup and/or determinative methods may require a solvent exchange prior to cleanup and/or determination.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for general quality control procedures and to Method 3500 for specific extraction and sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free solid matrix (e.g., reagent sand) method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted, or when there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement. This is especially important because of the possibility of interferences being extracted from the extraction cup seal.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Each analysis batch of 20 or less samples must contain: a method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, and a laboratory control sample, unless the determinative method provides other guidance. Also, routinely check the integrity of the instrument seals.

8.4 Surrogate standards must be added to all samples when specified in the appropriate determinative method.

9.0 METHOD PERFORMANCE

9.1 Multi-laboratory accuracy and precision data were obtained for PCBs in soil. Eight laboratories spiked Arochlors 1254 and 1260 into three portions of 10 g of Fuller's Earth on three non-consecutive days followed by immediate extraction using Method 3541. Six of the laboratories spiked each Arochlor at 5 and 50 mg/kg and two laboratories spiked each Arochlor at 50 and 500 mg/kg. All extracts were analyzed by Oak Ridge National Laboratory, Oak Ridge, TN, using Method 8081. These data are listed in a table found in Method 8081, and were taken from Reference 1.

9.2 Single-laboratory accuracy data were obtained for chlorinated hydrocarbons, nitroaromatics, haloethers, and organochlorine pesticides in a clay soil. The spiking concentrations ranged from 500 to 5000 µg/kg, depending on the sensitivity of the analyte to the electron capture detector. The spiking solution was mixed into the soil during addition and then immediately transferred to the extraction device and immersed in the extraction solvent. The data represents a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Methods 8081 for the organochlorine pesticides, 8091 for the nitroaromatics, 8111 for the hydrocarbons, and 8121 for the chlorinated hydrocarbons. These data are listed in a table located in their respective methods and were taken from Reference 2.

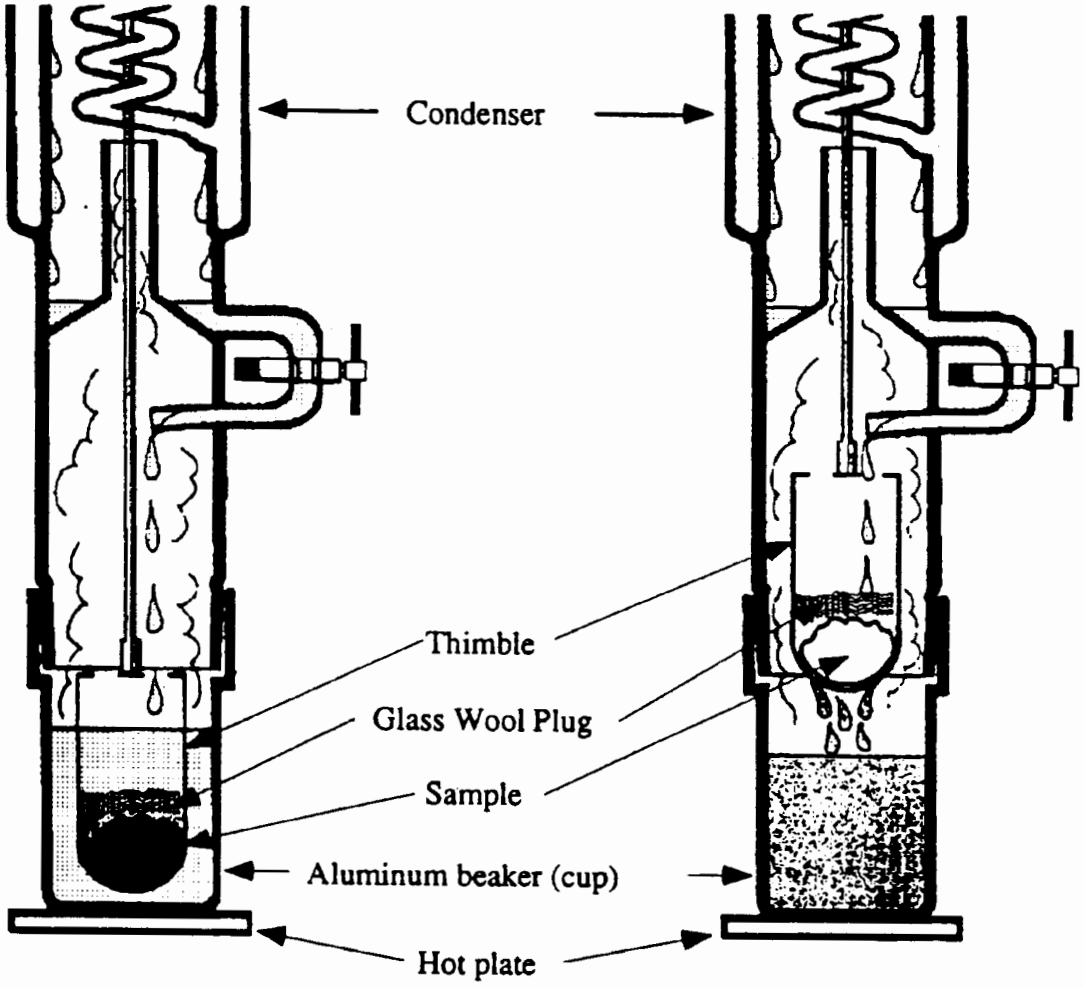
9.3 Single-laboratory accuracy and precision data were obtained for semivolatile organics in soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hr prior to extraction. Three determinations were performed and each extract was analyzed by gas chromatography/mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in a Table located in Method 8270 and were taken from Reference 2.

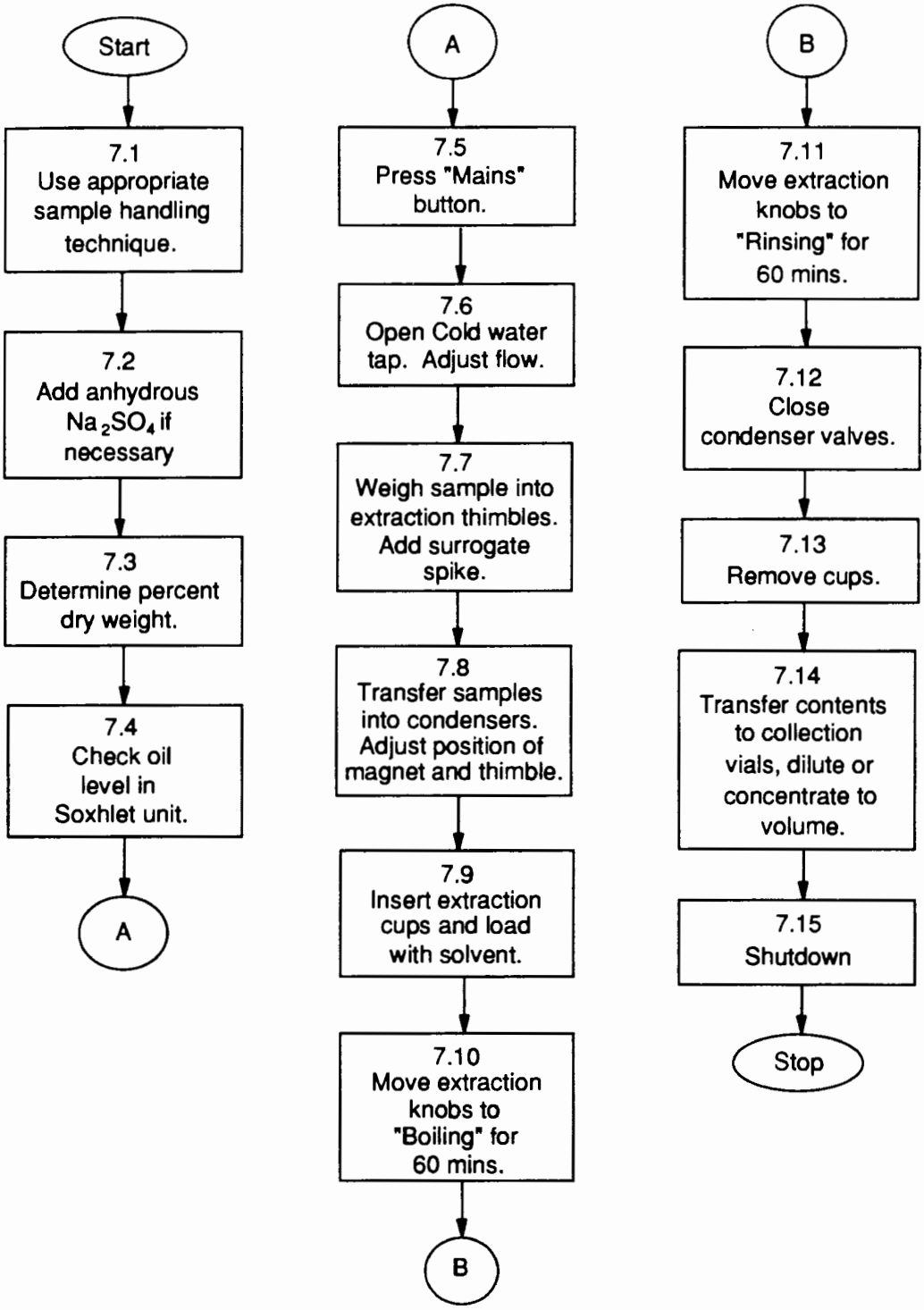
10.0 REFERENCES

1. Stewart, J. "Intra-Laboratory Recovery Data for the PCB Extraction Procedure"; Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6138; October 1989.

2. Lopez-Avila, V. (Beckert, W., Project Officer), "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments", EPA 600/X-91/140, US EPA, Environmental Monitoring Systems Laboratory-Las Vegas, October 1991.

Figure 1
Automated Soxhlet Extraction System




Start
7.1 Use appropriate sample handling technique.
7.2 Add anhydrous Na_2SO_4 if necessary
7.3 Determine percent dry weight.
7.4 Check oil level in Soxhlet unit.
A
A
7.5 Press "Mains" button.
7.6 Open Cold water tap. Adjust flow.
7.7 Weigh sample into extraction thimbles. Add surrogate spike.
7.8 Transfer samples into condensers. Adjust position of magnet and thimble.
7.9 Insert extraction cups and load with solvent.
7.10 Move extraction knobs to "Boiling" for 60 mins.
B
B
7.11 Move extraction knobs to "Rinsing" for 60 mins.
7.12 Close condenser valves.
7.13 Remove cups.
7.14 Transfer contents to collection vials, dilute or concentrate to volume.
7.15 Shutdown
Stop

EXTRACTION OF SEMIVOLATILE ANALYTES COLLECTED USING METHOD 0010 (MODIFIED METHOD 5 SAMPLING TRAIN)

1.0 SCOPE AND APPLICATION

1.1 This method describes the extraction of semivolatile organic compounds from samples collected by Method 0010. This method replaces Section 8.1 of Method 0010 (Modified Method 5 Sampling Train, also known as SemiVOST). Section 8.1 of Method 0010 addresses preparation of Method 0010 train components for analysis with very little detail.

1.2 Although this sample preparation technique is intended primarily for gas chromatography/mass spectrometric (GC/MS) analysis following Method 8270, the extracts prepared according to this method may be used with other analytical methods. The Method 0010 sampling train collects semivolatile organic compounds with boiling points above 100°C. Some of these semivolatile organic compounds may not be amenable to gas chromatography and will require the application of high performance liquid chromatography (HPLC) for quantitative analysis. The use of HPLC coupled with mass spectrometry (HPLC/MS) is an analytical technique that may also be applied. A solvent exchange from methylene chloride to a more polar solvent such as acetonitrile or extraction with a solvent other than methylene chloride will probably be required for successful application of HPLC techniques. Some semivolatile analytes may require derivatization for successful GC/MS analysis.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the extraction and concentration of semivolatile organic compounds from the components of Method 0010 trains. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Samples generated by the Method 0010 Sampling Train (Method 0010 Sampling Train, Figure 1) are separated into six parts:

a) a particulate matter filter (labeled in Method 0010 as Container No. 1);

b) a front half rinse (labeled in Method 0010 as Container No. 2);

c) condenser rinse and rinse of all sampling train components located between the filter and the sorbent module (labeled in Method 0010 as Container No. 5);

d) sorbent trap section of the organic module (labeled in Method 0010 as Container No. 3);

e) any condensate and condensate rinse (labeled in Method 0010 as Container No. 4); and

f) silica gel (labeled in Method 0010 as Container No. 6).

2.2 The overall sample preparation scheme (flowchart) is shown in Figure 3. The six parts recovered from the Method 0010 sampling train yield three 5-mL extracts to be analyzed according to the analytical procedures of Method 8270.

2.2.1 The particulate matter filter is extracted by Soxhlet (Method 3540, with exceptions as noted).

2.2.2 The front half rinse is filtered, and any filtrate is added to the particulate matter filter for Soxhlet extraction. The front half rinse is a 50:50 mixture of methanol and methylene chloride generated by rinsing the probe and the front half of the filter holder in the Method 0010 train. The front half rinse is extracted with methylene chloride by separatory funnel (Method 3510, with exceptions as noted) after sufficient organic-free reagent water has been added to make the methylene chloride separate as a distinct phase from the methanol/water.

2.2.3 The extracts from the filter and front half rinse are combined, moisture is removed by filtering through anhydrous sodium sulfate (Na_2SO_4), and the combined extract is concentrated using a Kuderna-Danish (K-D) sample concentrator (Method 3540) to a final volume of 5 mL. The final sample concentration to 5 mL can be performed more accurately by reducing the volume of the sample using a gentle stream of nitrogen or by using a micro-K-D.

2.2.4 The condensate and condensate rinse fractions consist of the aqueous contents of the first impinger of the Method 0010 sampling train and the 50:50 methanol/methylene chloride rinse of the first impinger of the Method 0010 sampling train. The condensate and condensate rinse fractions are combined and extracted with methylene chloride using a separatory funnel after sufficient organic-free reagent water has been added to make the methylene chloride separate from the methanol/water following the procedures of Method 3510 (with exceptions as noted).

2.2.5 After an initial methylene chloride extraction without pH adjustment, the pH of the combined condensate/condensate rinse fraction is determined. If the condensate/condensate rinse fraction is acid (pH < 7), the pH is adjusted to a level less than 2 and the methylene chloride extraction is repeated. The pH of the condensate/condensate rinse fraction is then made basic (pH > 12), and the methylene chloride extraction is repeated. The methylene chloride extracts are combined, and moisture is removed by filtration through a bed of anhydrous Na_2SO_4. If the condensate/condensate rinse fraction is found to be basic after the initial methylene chloride extraction, the pH adjustment sequence is reversed: a basic extraction is performed prior to an acid extraction, the methylene chloride extracts are combined, the moisture is removed, and the extract is concentrated to a volume of 5 mL.

2.2.6 The XAD-2® sampling module is combined with the filter holder back half rinse and the 50:50 methylene chloride/methanol condenser rinse and extracted by Soxhlet (Method 3540, with exceptions as noted). Organic-free reagent water is added to the extract to ensure the separation of methanol/water from the methylene chloride, and a water extraction of the methylene chloride extract is performed. Moisture is removed from the methylene chloride extract, which is then concentrated to a final volume of 5 mL for analysis.

2.2.7 The contents of the remaining impingers are usually archived, but may be extracted by separatory funnel. The silica gel is reused after regeneration by heating to remove moisture.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by preparing and analyzing laboratory method (or reagent) blanks.

3.1.1 Glassware must be cleaned thoroughly before using. The glassware should be washed with laboratory detergent in hot water followed by rinsing with tap water and distilled water. The glassware may be cleaned by baking in a glassware oven at 400°C for at least one hour. After the glassware has cooled, the glassware should be rinsed three times with methanol and three times with methylene chloride. Volumetric glassware should not be heated to 400°C. Rather, after washing and rinsing, volumetric glassware may be rinsed with methanol followed by methylene chloride and allowed to dry in air.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems in sample analysis.

3.2 Matrix interferences in the analysis may be caused by components of the sampling matrix that are extracted from the samples. If matrix interferences interfere with the analysis, sample cleanup procedures (e.g., Method 3620 or Method 3610) may be employed to remove or mitigate the interferences.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 50 mm I.D., with 500-mL round bottom flask and condenser. Larger equipment is acceptable if appropriate to the amount of sorbent.

4.2 Boiling chips - Polytetrafluoroethylene (PTFE), solvent rinsed with methylene chloride, approximately 10/40 mesh.

4.3 Forceps - Rinsed with methylene chloride before use.

4.4 Separatory funnel - 250-mL or larger, with PTFE stopcock.

4.5 Amber glass jar - 500-mL with PTFE-lined screw cap.

4.6 Glass funnel - Long stem.

4.7 Kuderna-Danish (K-D) apparatus.

4.7.1 Concentrator tube - 10-mL graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.7.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.7.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.7.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

NOTE: The glassware in Sec. 4.7 is recommended for the purpose of solvent recovery during the concentration procedures (Sec. 7.2.3 and 7.3.4) requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.8 Solvent vapor recovery system - (Kontes 545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.9 Glass wool - Non-silanized, pre-cleaned by Soxhlet extraction with methylene chloride. Air dry, store in pre-cleaned 500-mL jar.

4.10 Vials - 7- to 10-mL capacity, calibrated (calibrated centrifuge tubes may also be used).

4.11 Heating mantle - Rheostat-controlled.

4.12 Water bath - Heated, with concentric ring cover, capable of temperature control 80°C ± 5°C. The water bath should be used in a hood.

4.13 Gas-tight syringe - 5-mL to 10-mL capacity. Gas-tight syringes have a glass barrel, with a PTFE plunger to form an effective seal. The lack of contact with metal and the sealing properties make these syringes very useful for transferring liquid solutions.

4.14 Nitrogen blowdown apparatus - Analytical evaporator such as The Meyer N-EVAP Model 111 (Organomation Associates Inc., South Berlin, MA 01549) or equivalent.

4.15 Filter - Glass- or quartz-fiber filters, without organic binder. The filters should be the same as those used in the Method 0010 sampling train.

4.16 Wide range pH paper.

4.17 Rubber pipet filler bulb - for optional sorbent transfer procedure.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without compromising the integrity of the sample.

5.2 Methanol, CH_3OH - Pesticide quality or equivalent.

5.3 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.4 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.5 Sodium hydroxide solution (10 Molar) - Dissolve 40 g of sodium hydroxide (NaOH, ACS reagent grade) in organic-free reagent water and dilute to 100 mL.

5.6 Sulfuric acid (9 Molar), H_2SO_4 - Slowly add 50 mL of concentrated 18 M H_2SO_4 (ACS reagent grade, specific gravity 1.84) to 50 mL of organic-free reagent water.

5.7 Sodium sulfate, Na_2SO_4 - ACS, reagent grade, granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray.

5.8 Surrogate stock solution - Either surrogates (e.g., the surrogates used in Method 8270) or isotopically-labeled analogs of the compounds of interest should be spiked into the Method 0010 train components prior to extraction. Both surrogate and isotopically-labeled analogs may be used, if desired. A surrogate (i.e., a compound not expected to occur in an environmental sample but chemically similar to analytes) should be added to each sample, blank, and method spike just prior to extraction. The recovery of the surrogate is used to monitor for unusual matrix effects or sample processing errors. Normally three or more surrogates are added for each analyte group. The surrogate stock solution may be prepared from pure standard materials or purchased as a certified solution. Prepare the stock solution in methylene chloride, using assayed liquids or solids, as appropriate.

5.8.1 The following compounds are the surrogates recommended in Method 8270:

Acid	Base/Neutral
2-Fluorophenol	2-Fluorobiphenyl
2,4,6-Tribromophenol	Nitrobenzene-d_5
Phenol-d_6	Terphenyl-d_{14}

5.8.2 Prepare a surrogate stock solution in methylene chloride that contains the surrogate compounds at a concentration of 5000 µg/mL for the acidic compounds, and 2500 µg/mL for base/neutral compounds. Prepare the stock surrogate solution by accurately weighing 0.50 ± 0.05 g each of 2-fluorobiphenyl, p-terphenyl-d_{14}, and nitrobenzene-d_5, and 1.00 ± 0.05 g each of 2,4,6-tribromophenol, phenol-d_6, and 2-fluorophenol. Dissolve the materials in methylene chloride and dilute to volume in a 200-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution.

5.8.3 Transfer the stock solution into PTFE-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Stock solutions should be checked regularly for signs of degradation or evaporation, especially just prior to preparing spiking solutions. Allow solutions to come to room temperature before use.

5.8.4 Stock solutions should be replaced after one year, or sooner if analysis indicates a problem.

5.9 Surrogate spiking solution - Prepare a surrogate spiking solution by transferring a 10-mL aliquot of the surrogate stock solution (using a 10-mL volumetric pipet) into a 50-mL volumetric flask containing approximately 20 mL of methylene chloride. Dilute to a final volume of 50 mL with methylene chloride.

5.9.1 Transfer the surrogate spiking solution into PTFE-sealed screw-cap bottles appropriately sized to minimize headspace. Store at 4°C and protect from light. Spiking

solutions should be checked regularly for signs of degradation or evaporation, especially just prior to use.

5.9.2 Surrogate spiking solutions should be replaced after six months, or sooner if analysis indicates a problem.

5.10 Isotopically-labeled analog stock solution - Either surrogates (e.g., the surrogate standards used in Method 8270) or isotopically-labeled analogs of the compounds of interest must be spiked into the Method 0010 train components prior to extraction. Both surrogates and isotopically-labeled analogs may be used, if desired. The use of isotopically-labeled analogs is optional but highly recommended. Common isotopic labels which are used include deuterium and carbon-13; homologs and fluorinated analogs of the compounds of interest may also be used. To assess extraction efficiency, use of an isotopically-labeled analog of the compound of interest is essential. The isotopically-labeled analog is spiked into the matrix immediately prior to extraction, and losses of the spiked compound can be attributed to the sample extraction/concentration process. An isotopically-labeled analog stock solution can be made from pure standard materials or purchased as a certified solution. Even though the use of isotopically-labeled analogs is optional, each compound to be quantitated needs to be represented by a specific recovery standard, whether in the surrogate mixture (Sec. 5.8) or in a separate spike.

5.10.1 Prepare an isotopically-labeled analog stock solution by accurately weighing approximately 0.250 g of each of the materials to be used. Dissolve in methylene chloride and dilute to volume with methylene chloride in a 200-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution.

5.10.2 Transfer the stock solution into PTFE-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Stock solutions should be checked regularly for signs of degradation, evaporation, or isotope exchange, especially just prior to preparing spiking solutions from them. Allow solution to come to room temperature before use.

5.10.3 Stock solutions should be replaced after one year, or sooner if analysis indicates a problem.

5.11 Isotopically-labeled analog spiking solution

5.11.1 Prepare the isotopically-labeled analog standard by transferring a 10-mL aliquot of the stock isotopically-labeled analog stock solution (using a 10-mL volumetric pipet) into a 50-mL volumetric flask containing approximately 20 mL of methylene chloride. Dilute to volume with methylene chloride. The concentration of the spiking solution should allow the isotopically-labeled analogs to be observed in the final sample in approximately the middle of the calibration range for the gas chromatograph/mass spectrometer, assuming 100% recovery.

5.11.2 Transfer the solution into PTFE-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Spiking solutions should be checked regularly for signs of degradation or evaporation, especially just prior to use. Allow solutions to come to room temperature prior to use.

5.11.3 Spiking solutions should be replaced after six months, or sooner if analysis indicates a problem.

5.12 Stock method spike solution - A method spike consists of a spike of a clean matrix (i.e., clean, dry XAD-2®, clean, dry filter, or water) with a solution containing the compounds of interest (the method spike solution). The compound recoveries obtained from a method spike demonstrate that the compounds of interest can be recovered from the matrix, and aid in elucidating the effects of the field matrix. The method spike solution can be made from pure standard materials or purchased as certified solutions. The compounds of interest for the field test should be used as components of the method spike solution. A method spike is generated by spiking clean XAD-2® or clean organic-free reagent water.

5.12.1 Prepare a stock method spike solution by accurately weighing 0.05 g of each of the compounds of interest. Dissolve the materials in methylene chloride and dilute to volume in a 50-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution.

5.12.2 Transfer the stock method spike solution into PTFE-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Stock solutions should be checked regularly for signs of degradation or evaporation, especially just prior to preparing spiking solutions from them.

5.12.3 Stock solutions should be replaced after one year, or sooner if analysis indicates a problem.

5.13 Method spike standard solution

5.13.1 Prepare the method spike standard solution by transferring a 25-mL aliquot of the stock method spike solution (using a 25-mL volumetric pipet) into a 100-mL volumetric flask containing approximately 20 mL of methylene chloride. Dilute to volume with methylene chloride.

5.13.2 Transfer the method spike standard solution into PTFE-lined screw-cap bottles appropriately sized to minimize headspace. Store at 4°C and protect from light. Spiking solutions should be checked regularly for signs of degradation or evaporation, especially just prior to use.

5.13.3 Spiking solutions should be replaced after six months, or sooner if analysis indicates a problem.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 The six components from each Method 0010 sampling train (Figure 1) should be stored at 4°C between the time of sampling and extraction.

6.2 Each sample should be extracted within 14 days of collection and analyzed within 40 days of extraction. The extracted sample should be stored at 4°C.

7.0 PROCEDURE

7.1 The sample preparation procedure for the six parts of the Method 0010 train will result in three sample extracts for analysis:

a) Particulate matter filter and front half rinse;
b) Condensate and condensate rinse; and
c) XAD-2® and condenser/back half rinse.

7.2 Particulate matter filter and front half rinse

7.2.1 Filter - The filter is identified as Container No. 1 in Method 0010.

7.2.1.1 Using clean forceps, place about 10 PTFE boiling chips into the bottom of the round bottom flask of the Soxhlet extractor and connect the Soxhlet extractor to the round bottom flask.

7.2.1.2 Using a clean syringe or volumetric pipet, add a 1-mL aliquot of the surrogate spiking solution (Sec. 5.9) to the filter. If isotopically-labeled analogs are being used, the isotopically-labeled analog solution (Sec. 5.11) may be added at this time. If a method spike is being prepared, the method spike solution (Sec. 5.13) may be added at this time.

7.2.1.2.1 To ensure proper filter spiking, use a volume of approximately 1 mL of spiking solution. Leave the filter in the petri dish, particulate material on top, for spiking. Add the 1 mL of spiking solution uniformly onto the particulate-coated surface of the filter in the petri dish by spotting small volumes at multiple filter locations, using a syringe.

7.2.1.2.2 Repeat the spiking process with isotopically-labeled standards or method spike solution, if these solutions are being used.

7.2.1.3 Using clean forceps, place the particulate matter filter into a glass thimble and position the glass thimble in the Soxhlet extractor, making sure that the filter will be completely submerged in the methylene chloride with each cycle of the Soxhlet extractor. Place a piece of pre-cleaned unsilanized glass wool on top of the filter in the Soxhlet extractor to keep the filter in place. Rinse the petri dish three times with methylene chloride and add rinses to the Soxhlet.

7.2.1.4 The front half rinse (Container No. 2) may contain particulate material which has been removed from the probe. This particulate material should be extracted with the filter.

7.2.1.4.1 To separate particulate matter from the front half rinse, filter the front half rinse. To avoid introducing any contamination, use the same type of filter which has been used in the Method 0010 train, from the same lot as the filter in the Method 0010 train. Filter the Front Half Rinse, rinse Container No. 2 three times with 10-mL aliquots of methylene chloride, and filter the methylene chloride rinses.

7.2.1.4.2 Transfer the filter with any particulate matter to the Soxhlet extractor with the original filter from the Method 0010 train. Extract the two filters together.

7.2.1.4.3 Return the liquid portion of Container No. 2 to its original container for subsequent extraction or, alternatively, the front half rinse can be

filtered directly into a separatory funnel for extraction of the liquid portion of the front half rinse.

7.2.1.5 Slowly add methylene chloride to the Soxhlet extractor containing the two filters through the Soxhlet (with condenser removed), allowing the Soxhlet to cycle. Add sufficient solvent to fill the round bottom flask approximately half full and submerge the thimble containing the filters.

7.2.1.6 Place a heating mantle under the round bottom flask and connect the upper joint of the Soxhlet to a condenser, making sure that the coolant is flowing through the condenser.

7.2.1.7 Allow the sample to extract for 18 hours, adjusting the mantle temperature for cycling (flushing solvent from the Soxhlet into the round bottom flask) approximately once every thirty minutes.

7.2.1.8 After cooling, disconnect the extractor from the condenser. Tilt the Soxhlet slightly until the remaining solvent has drained into the round bottom flask.

7.2.1.9 Transfer the extract from the round bottom flask into a 500-mL amber glass bottle with PTFE-lined screw cap. The bottle should have been rinsed three times each with methanol and methylene chloride. Rinse the round bottom flask three times with approximately 10-mL aliquots of methylene chloride and transfer the rinses to the amber bottle. Store the filter extract at 4°C until extraction of the filtered front half rinse has been completed.

7.2.2 Front half rinse - The front half rinse is identified as Container No. 2 in Method 0010.

7.2.2.1 Transfer the liquid contents of the filtered front half rinse sample to a separatory funnel of appropriate size for the volume of the sample (a typical front half rinse sample is 200 to 300 mL). Rinse the sample container three times with 10-mL aliquots of methylene chloride, transferring the rinses to the separatory funnel after each rinse.

7.2.2.2 Because the front half rinse sample consists of a mixture of methanol and methylene chloride, sufficient organic-free reagent water must be added to the separatory funnel to cause the organic and aqueous/methanol phases to separate into two distinct layers. The methylene chloride layer will be at the bottom of the separatory funnel. Continue to add water until the bottom layer (methylene chloride) does not increase in volume. An increase in volume can be monitored by marking the separatory funnel at the position of the phase separation.

NOTE: The front half rinse is not spiked with any surrogate, isotopic analog, or method spike solutions because the extract from the front half rinse is combined with the extract from the particulate matter filter sample.

7.2.2.3 Add additional methylene chloride, if necessary, so that the ratio of water/methanol to methylene chloride is approximately 3:1. Add sodium hydroxide (Sec. 5.5) until pH of the water layer is > 11 (but < 14). Use wide-range pH paper to determine pH. Shake vigorously for 2 minutes with rapid arm motion, with periodic venting to release excess pressure. Allow the organic layer to separate for at least 10 minutes.

Collect the methylene chloride extract in a 500-mL amber glass bottle with PTFE-lined screw cap, which has been rinsed three times each with methanol and methylene chloride.

7.2.2.4 Add a second volume of methylene chloride (approximately the same volume as the first extraction) to the separatory funnel and repeat the extraction procedure, combining the methylene chloride extracts in the amber bottle.

7.2.2.5 Perform a third extraction in the same manner.

7.2.2.6 Acidify the water to a pH <2 (but > 0) with sulfuric acid (Sec. 5.6) and repeat Sec. 7.2.2.4 three times. Measure pH with wide-range pH paper.

7.2.3 Concentration of filter and front half rinse extracts - The combined extracts and rinses of extract storage bottles will have a total volume of 1 liter or more.

7.2.3.1 Assemble a Kuderna-Danish concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask with clips or springs. Using a clean pair of forceps, place about five PTFE boiling chips into the concentrator tube. If the volume of extract to be concentrated is greater than 500 mL, repeat the concentration as many times as required using the same 500-mL evaporative flask and systematically adding remaining extract (allow to cool slightly before addition of more extract). If repeated concentrations are performed, use new boiling chips each time.

7.2.3.2 Using a clean pair of forceps, place a small portion of precleaned unsilanized glass wool in the bottom of a long stemmed glass funnel (147 mm diameter), and pour a 2.54-cm (1-in) layer of cleaned sodium sulfate (Sec. 5.7) on top of the glass wool (use more sodium sulfate, if possible; fill the funnel to within approximately 1.27 cm (0.5 in) of the top).

7.2.3.3 Rinse the sodium sulfate contained in the funnel three times with methylene chloride; discard the rinses. Support the funnel in a ring or clamp above the flask to prevent tipping.

7.2.3.4 Place the funnel into the upper opening of the K-D flask and slowly pour extracts from the Filter and Front Half Rinse through the sodium sulfate. Rinse the amber jars containing the extracts three times, using approximately 10 mL of methylene chloride each time. Add the rinses to the funnel. Rinse the sodium sulfate with methylene chloride to complete the transfer.

NOTE: During this process, monitor the condition of the sodium sulfate to determine that the bed of sodium sulfate is not solidifying and exceeding its drying capacity. If the sodium sulfate bed can be stirred and is still free-flowing, effective moisture removal from the extracts is occurring. If the sodium sulfate bed has begun to solidify, do not add more extract. Replace the sodium sulfate bed, re-dry the contents of the K-D flask, and continue drying the extracts.

7.2.3.5 Attach a three-ball macro Snyder column to the evaporative flask. Prewet the Snyder column by adding about 2 mL of methylene chloride to the top. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the K-D apparatus, following manufacturer's instructions. Place the K-D

apparatus on a hot water bath (80 - 85°C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 20 to 30 minutes. Rinse sides of K-D during concentration with a small volume of methylene chloride. When the apparent volume of the liquid reaches 6-8 mL, remove the K-D apparatus from the water bath and allow the apparatus to cool and drain for at least 10 minutes.

NOTE: Never let the extract in the concentrator tube go to dryness even though additional solvent is present in the upper portion of the K-D apparatus.

NOTE: If the sample concentration is not completed within the anticipated period of time, check the temperature of the water bath and check the composition of the sample. If the methanol has not been completely removed from the methylene chloride extract by the procedures described in Secs. 7.2.2.2 and 7.2.2.3, residual methanol will concentrate far slower than a methylene chloride extract and analytes will be lost in the concentration step. A sample containing methanol which has been concentrating for a prolonged period of time cannot be recovered, but extracts which contain residual methanol and have not yet been concentrated can be recovered by performing the procedures in Secs. 7.2.2.2 and 7.2.2.3 again.

7.2.3.6 Remove the Snyder column and evaporative flask. With a clean pair of forceps, add two new PTFE boiling chips to the concentrator tube. Attach a two-ball micro Snyder column to the concentrator tube. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the K-D apparatus, following manufacturer's instructions. Prewet the Snyder column with about 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in hot water, supporting the tube with a clamp. When the apparent volume of the liquid reaches 4 - 5 mL, remove the K-D apparatus from the water bath and allow the apparatus to cool and drain for at least 10 minutes. If the volume is greater than 5 mL, add a new boiling chip to the concentrator tube, prewet the Snyder column, and concentrate again on the hot water bath. Wipe moisture from the outside of the concentrator tube. Transfer the extract to a calibrated vial or centrifuge tube, rinse concentrator tube with a minimum volume of methylene chloride and add rinses to the vial, and add methylene chloride, if necessary, to attain a final volume of 5 mL.

Alternatively, the final concentration may be performed by blowing the surface of the solvent with a gentle stream of nitrogen using a glass disposable pipet to direct the stream of nitrogen. When the nitrogen blowdown technique is used, care must be taken to carefully rinse the sides of the vessel using a minimum quantity of methylene chloride to ensure that analytes are in the methylene chloride solution, not deposited on the sides of the glass container. Perform the blowdown procedure in a calibrated vial or centrifuge tube which does not contain boiling chips. The final extract volume must be 5 mL.

7.2.3.7 Transfer the extract to a 10-mL glass storage vial with a PTFE-lined screw cap. Label the extract as Front Half Rinse and Particulate Filter, and store at 4°C until analysis (Sec. 7, Method 8270). Mark the liquid level on the vial with a permanent marker to monitor solvent evaporation during storage.

7.3 Condensate and condensate rinse - The condensate is identified as Container No. 4 in Method 0010; the condensate rinse is Container No. 5.

7.3.1 Transfer the contents of both the condensate and the condensate rinse samples to a clean separatory funnel (expected volume of both containers is approximately 500 mL). Rinse each of the sample containers with three aliquots of methylene chloride (approximately 10 mL each), transferring the rinses to the separatory funnel.

7.3.2 Using a clean syringe or volumetric pipet, add a 1-mL aliquot of the surrogate solution (Sec. 5.9) to the liquid in the separatory funnel. If isotopically-labeled analogs are being used, the isotopically-labeled analog solution (Sec. 5.11) should be added to the separatory funnel.

7.3.3 Perform an initial methylene chloride extraction of the combined condensate/condensate rinse which has been spiked with appropriate spiking solution(s). Add organic-free reagent water as needed to ensure separation of phases. After extraction three times with methylene chloride, check the pH of the condensate/condensate rinse solution with wide-range pH paper.

7.3.3.1 If the solution is acidic (pH < 7), add acid until the pH is < 2 but > 0 and perform another methylene chloride extraction. Then make the condensate/condensate rinse solution basic (pH > 11 but < 14) and perform another methylene chloride extraction. Combine the methylene chloride extracts from all pH levels, remove moisture, and concentrate for analysis.

7.3.3.2 If, after the initial methylene chloride extraction, the condensate/condensate rinse solution is basic, increase pH until the pH is > 11 but < 14, and perform another methylene chloride extraction. Then make the condensate/condensate rinse solution acidic (pH < 2 but > 0) and perform another methylene chloride extraction. Combine the methylene chloride extracts from all pH levels, remove moisture, and concentrate the extract for analysis.

7.3.4 Refer to Sec. 7.2.2.2 and following sections for extraction and concentration of the condensate/condensate rinse extract.

7.4 XAD-2® - The sorbent trap section of the organic module is identified as Container No. 3 in Method 0010. The sorbent trap section of the organic module shall be used as a sample transport container.

7.4.1 Using clean forceps, place about 10 PTFE boiling chips in the bottom of the round bottom flask of the Soxhlet extractor and connect the Soxhlet extractor to the round bottom flask.

7.4.2 Transfer the XAD-2® to the extraction thimble. Remove the glass wool plug from the XAD-2® trap and add to the thimble of the Soxhlet extractor. If ground glass stoppers are used to seal the sorbent trap during shipment, these ground glass stoppers should be rinsed with methylene chloride and the rinsate added to the round bottom flask of the Soxhlet extractor.

7.4.2.1 If the XAD-2® is dry (i.e., free-flowing), pour the XAD-2® directly into the thimble (or directly into the Soxhlet extractor) and rinse the trap with methylene chloride, adding the rinses to the round bottom flask.

7.4.2.2 If the XAD-2® is wet, removal from the trap may be difficult. To accomplish the transfer, flush the resin from the trap using a PTFE wash bottle containing methylene chloride. Alternatively, acidic water (pH < 2) can be used to wash the walls of the XAD-2® trap. Collect the resin and solvent in a clean 500-mL beaker. Transfer the XAD-2®/methylene chloride from the beaker to the extraction thimble, taking care that no solvent is lost. Alternatively, the XAD-2® can be transferred directly to the Soxhlet extractor and the methylene chloride rinse and transfer solvent allowed to drain through the XAD-2® to the round bottom flask. Rinse the beaker several times with methylene chloride, pouring the rinses through the XAD-2® bed once the extraction thimble is in the Soxhlet extractor. Be sure that a glass wool plug is in place above the XAD-2® to ensure that the XAD-2® does not float out of the thimble.

NOTE: Under no circumstances should methanol or acetone be used to transfer the resin.

7.4.2.3 Alternative approaches to transfer of XAD-2® from the trap to the extraction thimble are discussed below.

7.4.2.3.1 The XAD-2® can be transferred directly to the Soxhlet extractor and the methylene chloride rinse and transfer solvent allowed to drain through the XAD-2® to the round bottom flask. If ground glass stoppers are used to seal the sorbent trap during shipment, these ground glass stoppers should be rinsed with methylene chloride and the rinsate added to the round bottom flask of the Soxhlet extractor. To remove the XAD-2® from the sampling module, remove the glass wool from the end of the XAD-2® sampling module. Place this glass wool in the Soxhlet extractor to ensure thorough extraction of the glass wool. If the XAD-2® is being transferred directly to the Soxhlet extractor, place a small piece of pre-cleaned glass wool in the side-arm of the Soxhlet extractor to ensure that no XAD-2® enters the side-arm of the Soxhlet extractor. Invert the XAD-2® sampling module (glass frit up) over an extraction thimble contained in a beaker, or directly over the Soxhlet extractor with pre-cleaned glass wool in the bottom, as shown in Figure 2. Add approximately 5 to 10 mL of methylene chloride above the glass frit of the sampling module. Connect a rubber pipet filler bulb with check valve that has been fitted with a ball joint to the XAD-2® sampling module. Using air pressure created by squeezing the bulb, gently but firmly push the methylene chloride through the frit, forcing the XAD-2® out of the sampling module. Avoid allowing methylene chloride to be pulled up into the bulb, since the sample will be compromised if methylene chloride is pulled up into the bulb and allowed to become part of the extract. This process will need to be repeated 3 to 5 times. Use a PTFE wash bottle containing methylene chloride to rinse the walls of the sampling module to transfer XAD-2® which has been retained on the walls of the sampling module after transfer of XAD-2® to the Soxhlet. A methylene chloride rinse of the walls will not remove all of the XAD-2®, but after 3 to 5 rinses of the walls of the sampling module, no more than a monolayer of XAD-2® particles should be retained. If more than a monolayer of XAD-2® remains, additional rinses are required. The glass wool in the side arm of the Soxhlet extractor must be removed and added to the Soxhlet.

NOTE: Under no conditions should methanol or acetone be used in the transfer of the XAD-2®.

7.4.2.3.2 Alternatively, the wet XAD-2® may be transferred from the sampling module to a piece of cleaned aluminum foil by inverting the trap (glass frit up) and tapping the trap on a solid surface covered with the cleaned aluminum foil. This process is slow and may result in breakage of the sampling module. If ground glass stoppers are used to seal the sorbent trap during shipment, these ground glass stoppers should be rinsed with methylene chloride and the rinsate added to the round bottom flask of the Soxhlet extractor. After the majority of the XAD-2® has been removed from the trap by tapping, the XAD-2® on the aluminum foil may be transferred to the extraction thimble. The sampling module should be rinsed with methylene chloride to flush the remaining XAD-2® particles adhering to the glass wall into the extraction thimble. After all XAD-2® has been transferred into the Soxhlet thimble, add a plug of glass wool to the top of the XAD-2® to hold the resin in place.

7.4.3 With the XAD-2® in the Soxhlet extractor and glass wool on top of the XAD-2®, use a clean syringe or volumetric pipet to add a 1-mL aliquot of the surrogate spiking solution to the XAD-2®. Be sure that the needle of the syringe penetrates the XAD-2® bed to a depth of at least 1.27 cm (0.5 in). If isotopically-labeled standard solution or method spike solution is being used, these solutions should be spiked at this time.

7.4.4 Container No. 5 contains the methylene chloride/methanol rinse of the condenser and all train components from the back half of the filter holder to the XAD-2® sampling module. These rinses consist of 50:50 methanol:methylene chloride. Transfer the contents of Container No. 5 to a separatory funnel and rinse the container with three 10-mL aliquots of methylene chloride. Add the rinses to the separatory funnel. Sufficient organic-free reagent water must be added to the separatory funnel to cause the organic and aqueous phases to separate into two distinct layers. Refer to Sec. 7.2.2.2 and following sections for preparation of a methylene chloride extract from Container No. 5. Add the methylene chloride layer from the separatory funnel directly to the Soxhlet extractor containing the XAD-2® or collect the methylene chloride extract in a container and transfer from this container to the Soxhlet containing the XAD-2®. Pour the methylene chloride extract of the condenser and back half rinses through the XAD-2® in the Soxhlet extractor; rinse the container or separatory funnel 3 times with approximately 10-mL aliquots of methylene chloride and add the rinses to the Soxhlet.

7.4.5 Add additional methylene chloride to the Soxhlet extractor, if necessary, pouring approximately 300-400 mL through the XAD-2® bed so that the round bottom flask is approximately half-full and the XAD-2® bed is covered.

7.4.6 Place a heating mantle under the round bottom flask and connect the upper joint of the Soxhlet extractor to a condenser.

NOTE: Start the extraction process immediately after surrogate/analog spiking is completed to ensure that no volatilization of organic compounds from the resin or any spiking solutions occurs before the extraction process is started.

7.4.7 Allow the sample to extract for at least 18 hours but not more than 24 hours, cycling once every 25 - 30 minutes.

NOTE: Be sure that cooling water for the condensers is cold and circulating. Watch the extractor through two or three cycles to ensure that the extractor is working properly.

7.4.8 After the Soxhlet extractor has been cooled, disconnect the extractor from the condenser and tilt the extractor slightly until the remaining solvent in the Soxhlet has drained into the round bottom flask.

7.4.9 Inspect the contents of the round bottom flask to determine whether there is a visible water layer on top of the methylene chloride. If no water layer is observed, transfer the extract into a 500-mL amber glass bottle with PTFE-lined screw cap for storage (Sec. 7.2.1.8), or proceed directly with removal of moisture and concentration of the extract (Sec. 7.2.3.1). If a water layer is observed in the Soxhlet round bottom flask, transfer the contents to a separatory funnel, rinsing the round bottom flask three times with methylene chloride and adding the rinsings to the separatory funnel. Drain the methylene chloride from the separatory funnel and store in an amber glass bottle. Then perform an acid/base extraction of the water layer remaining in the separatory funnel (Sec. 7.3.3). Add the methylene chloride extract from the acid/base extraction to the methylene chloride extract from the round bottom flask in the amber glass jar. Store the extract in the amber glass bottle at 4°C for subsequent removal of moisture and concentration following the steps outlined in Sec. 7.2.3.1.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific Quality Control procedures.

8.2 A method blank consists of a clean filter, clean dry XAD-2®, or organic-free reagent water, which is spiked with surrogates prior to extraction. The method blank is extracted and concentrated using the same procedures as the corresponding sample matrix. One method blank is extracted and analyzed for every ten samples.

8.3 A method spike consists of a clean filter, XAD-2®, or organic-free reagent water, which is spiked with surrogates, isotopically-labeled standards, if used, and method spike solution, if used, prior to extraction. The method spike is extracted and concentrated using the same procedures as the corresponding sample matrix. At least one method spike is extracted and analyzed for every matrix, with a frequency of one method spike for every twenty samples.

9.0 METHOD PERFORMANCE

9.1 Method Performance Evaluation - Evaluation of analytical procedures for a selected series of compounds must include the sample preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through all the procedures.

9.2 Method Detection Limits - The overall method detection limits (lower and upper) need to be determined on a compound-by-compound basis because different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrument minimum detection limits. The method detection limit needs to be quoted relative to a given sample volume. The upper limits for the method need to be determined relative to compound retention volumes (breakthrough).

9.3 Method Precision and Bias - The overall method precision and bias needs to be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and

extraction efficiency of the train components. The surrogate recoveries shown below represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

10.0 REFERENCES

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2. Handbook. Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration, EPA-625/6-89-023, Cincinnati, OH. 1990.

3. Bursey, J., Merrill, R., McAllister, R., and McGaughey, J., Laboratory Validation of VOST and SemiVOST for Halogenated Hydrocarbons from the Clean Air Act Amendments List, Vols. 1 and 2, U. S. Environmental Protection Agency, EPA 600/R-93/123a and b, (NTIS PB93-227163 and PB93-227171) Research Triangle Park, NC. July. 1993.

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TABLE 1

PRECISION AND BIAS VALUES FOR METHOD 3542[1]

Compound	Mean Recovery	Standard Deviation	Relative Standard Deviation (%)
2-Fluorophenol	74.6	28.6	38.3
Phenol-d_5	77.8	27.7	35.6
Nitrobenzene-d_5	65.6	32.5	49.6
2-Fluorobiphenyl	75.9	30.3	39.9
2,4,6-Tribromophenol	67.0	34.0	50.7
Terphenyl-d_{14}	78.6	32.4	41.3

[1] The surrogate recovery values shown in Table 1 represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

FIGURE 1

METHOD 0010 SAMPLING TRAIN

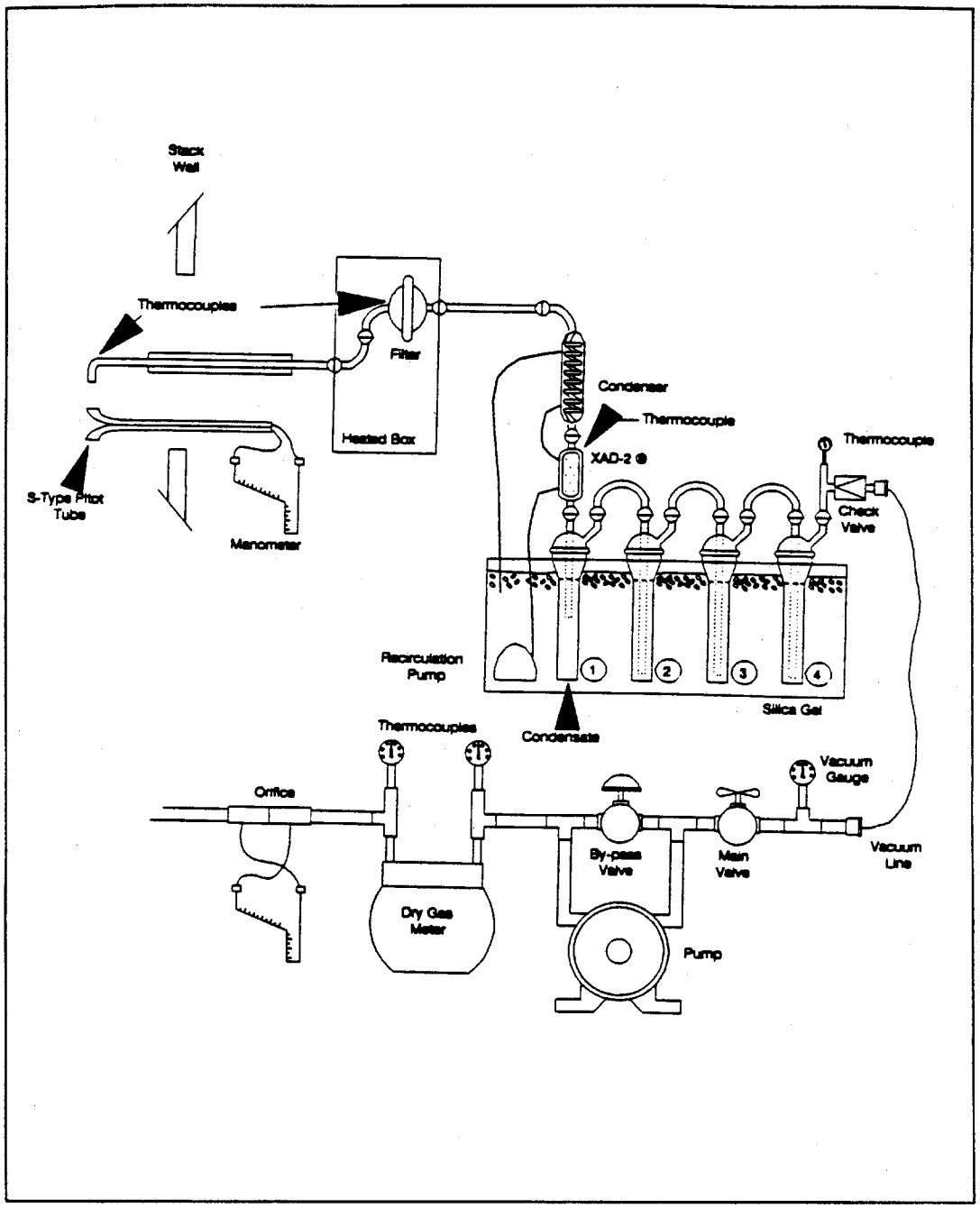


FIGURE 2

TRANSFER OF WET XAD-2®

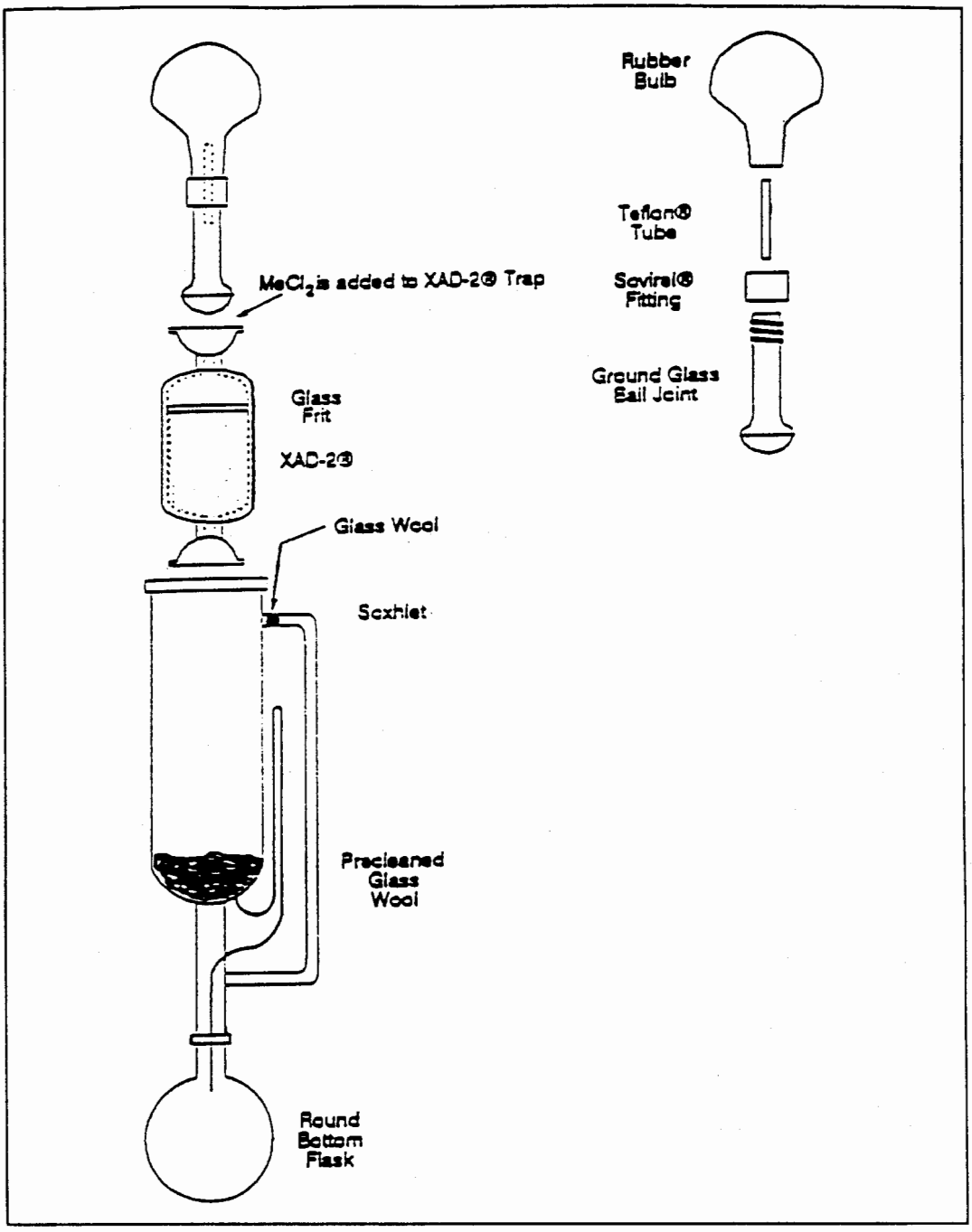


FIGURE 3

SAMPLE PREPARATION FLOWCHART USING METHOD 0010
(MODIFIED METHOD 5) SAMPLING TRAIN

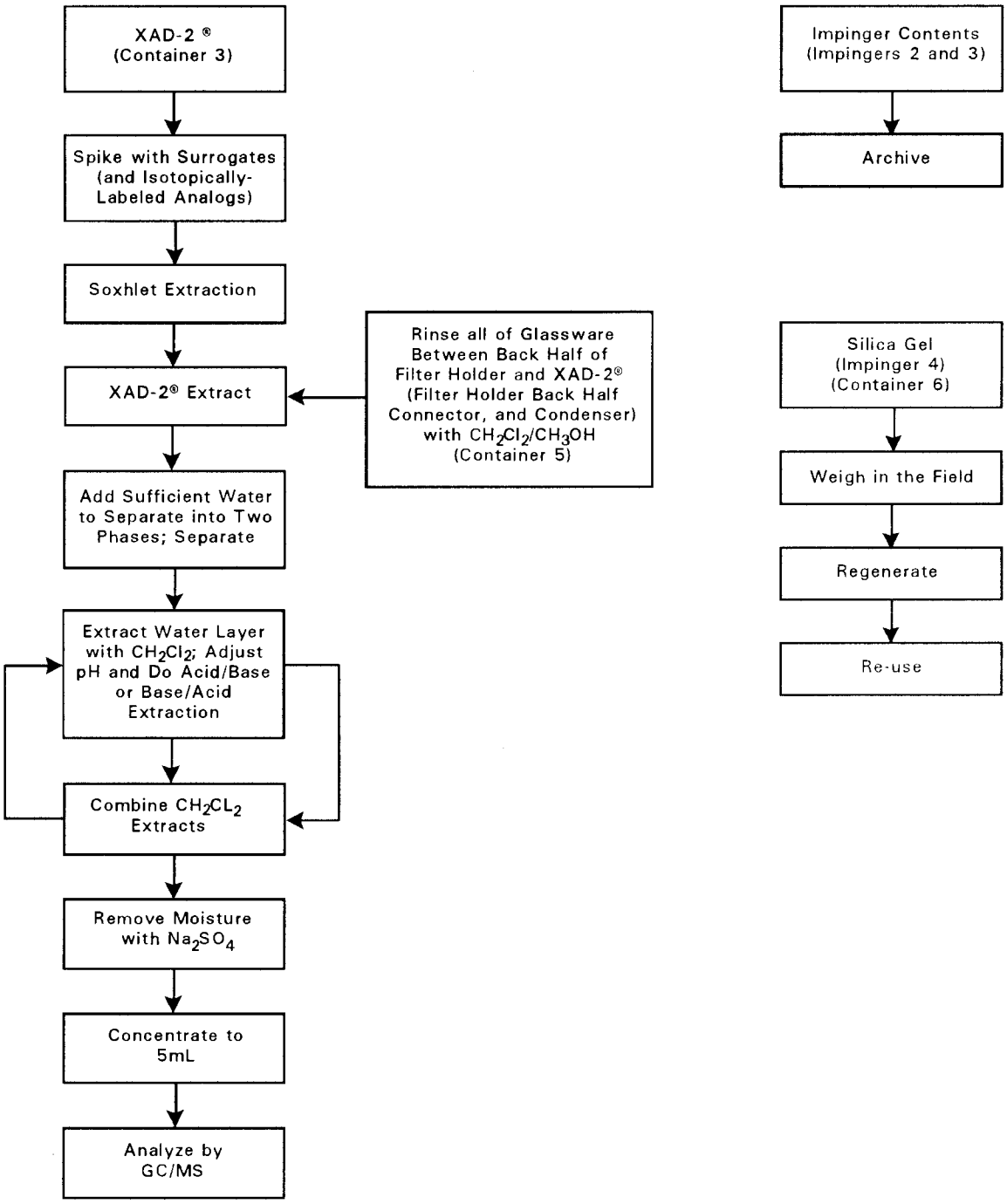
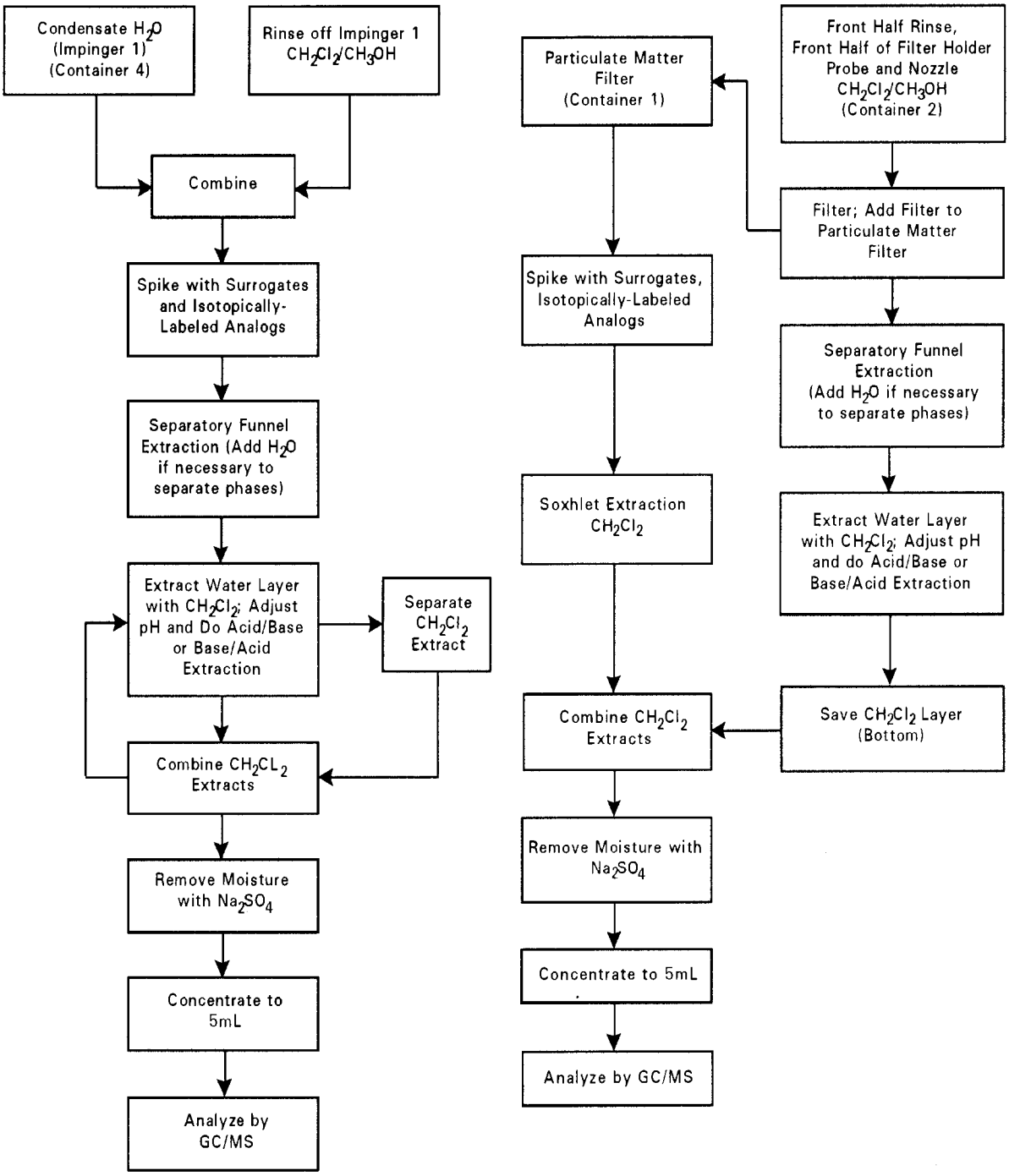


FIGURE 3 (continued)

SAMPLE PREPARATION FLOWCHART USING METHOD 0010
(MODIFIED METHOD 5 SAMPLING TRAIN)



METHOD 3545

PRESSURIZED FLUID EXTRACTION (PFE)

1.0 SCOPE AND APPLICATION

1.1 Method 3545 is a procedure for extracting water insoluble or slightly water soluble semivolatile organic compounds from soils, clays, sediments, sludges, and waste solids. The method uses elevated temperature (100°C) and pressure (1500 - 2000 psi) to achieve analyte recoveries equivalent to those from Soxhlet extraction, using less solvent and taking significantly less time than the Soxhlet procedure. This procedure was developed and validated on a commercially-available, automated extraction system.

1.2 This method is applicable to the extraction of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, and PCBs, which may then be analyzed by a variety of chromatographic procedures.

1.3 This method has been validated for solid matrices containing 250 to 12,500 µg/kg of semivolatile organic compounds, 250 to 2500 µg/kg of organophosphorus pesticides, 5 to 250 µg/kg of organochlorine pesticides, 50 to 5000 µg/kg of chlorinated herbicides, and 1 to 1400 µg/kg of PCBs. The method may be applicable to samples containing these analytes at higher concentrations and may be employed after adequate performance has been demonstrated for the concentrations of interest (see Method 3500, Sec. 8.0).

1.4 This method is applicable to solid samples only, and is most effective on dry materials with small particle sizes. Therefore, waste samples must undergo phase separation, as described in Chapter Two, and only the solid phase material is to be extracted by this procedure. If possible, soil/sediment samples may be air-dried and ground to a fine powder prior to extraction. Alternatively, if the loss of analytes during drying is a concern, soil/sediment samples may be mixed with anhydrous sodium sulfate or pelletized diatomaceous earth. The total mass of material to be prepared depends on the specifications of the determinative method and the sensitivity required for the analysis, but 10 - 30 g of material are usually necessary and can be accommodated by this extraction procedure.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared for extraction either by air drying the sample, or by mixing the sample with anhydrous sodium sulfate or pelletized diatomaceous earth. The sample is then ground to a 100 - 200 mesh powder (150 µm to 75 µm) and loaded into the extraction cell.

2.2 The extraction cell containing the sample is heated to the extraction temperature (see Sec. 7.8), pressurized with the appropriate solvent system, and extracted for 5 minutes (or as recommended by the instrument manufacturer). The solvent systems used for this procedure vary with the analytes of interest and are described in Sec. 5.5.

2.3 The solvent is collected from the heated extraction vessel and allowed to cool.

2.4 The extract may be concentrated, if necessary, and, as needed, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 If necessary, Florisil and/or sulfur cleanup procedures may be employed. In such cases, proceed with Method 3620 and/or Method 3660.

4.0 APPARATUS AND MATERIALS

4.1 Pressurized fluid extraction device

4.1.1 Dionex Accelerated Solvent Extractor or Supelco SFE-400 with appropriately-sized extraction cells. Currently, cells are available that will accommodate 10-g, 20-g and 30-g samples. Cells should be made of stainless steel or other material capable of withstanding the pressure requirements (2000+ psi) necessary for this procedure.

4.1.2 Other system designs may be employed, provided that adequate performance can be demonstrated for the analytes and matrices of interest.

4.2 Apparatus for determining percent dry weight

4.2.1 Oven - drying

4.2.2 Desiccator

4.2.3 Crucibles - porcelain or disposable aluminum

4.3 Apparatus for grinding - capable of reducing particle size to < 1 mm.

4.4 Analytical balance - capable to weighing to 0.01 g.

4.5 Vials for collection of extracts - 40-mL or 60-mL, pre-cleaned, open top screw-cap with PTFE-lined silicone septum (Dionex 049459, 049460, 049461, 049462 or equivalent).

4.6 Filter disk - 1.91 cm, Type D28 (Whatman 10289356, or equivalent).

4.7 Cell cap sealing disk (Dionex 49454, 49455, or equivalent).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Drying agents

5.3.1 Sodium sulfate (granular anhydrous), Na_2SO_4.

5.3.2 Pelletized diatomaceous earth.

5.3.3 The drying agents should be purified by heating at 400°C for 4 hours in a shallow tray, or by extraction with methylene chloride. If extraction with methylene chloride is employed, then a reagent blank should be prepared to demonstrate that the drying agent is free of interferences.

5.4 Phosphoric acid solution (see Sec. 5.5.5). Prepare a 1:1 (v/v) solution of 85% phosphoric acid (H_3PO_4) in organic-free reagent water.

5.5 Extraction solvents

The extraction solvent to be employed depends on the analytes to be extracted, as described below. All solvents should be pesticide quality or equivalent. Solvents may be degassed prior to use.

5.5.1 Organochlorine pesticides may be extracted with acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14} or acetone/methylene chloride (1:1,v/v), CH_3COCH_3/CH_2Cl_2 .

5.5.2 Semivolatile organics may be extracted with acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2 or acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}.

5.5.3 PCBs may be extracted with acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14} or acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2 or hexane, C_6H_{14}.

5.5.4 Organophosphorus pesticides may be extracted with methylene chloride, CH_2Cl_2 or acetone/methylene chloride (11:1, v/v), CH_3COCH_3/CH_2Cl_2.

5.5.5 Chlorinated herbicides may be extracted with an acetone/methylene chloride/phosphoric acid solution (250:125:15, v/v/v), $CH_3COCH_3/CH_2Cl_2/H_3PO_4$, or an acetone/methylene chloride/trifluoroacetic acid solution (250:125:1, v/v/v), $CH_3COCH_3/CH_2Cl_2/CF_3COOH$. (If the second option is used, the trifluoroacetic acid solution should be prepared by mixing 1% trifluoroacetic acid in acetonitrile.) Make fresh solutions before each batch of extractions.

5.5.6 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest in the sample matrix (see Method 3500, Sec. 8.0).

CAUTION: For best results with very wet samples (e.g., ≥30% moisture), reduce or eliminate the quantity of hydrophilic solvent used.

5.6 High-purity gases such as nitrogen, carbon dioxide, or helium are used to purge and/or pressurize the extraction cell. Follow the instrument manufacturer's recommendation for the choice of gases.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analysis, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Air dry the sample at room temperature for 48 hours in a glass tray or on hexane-rinsed aluminum foil. Alternatively, mix the sample with an equal volume of anhydrous sodium sulfate or pelletized diatomaceous earth until a free-flowing powder is obtained.

NOTE: Dry, finely-ground soil/sediment allows the best extraction efficiency for nonvolatile, nonpolar organics, e.g., 4,4'-DDT, PCBs, etc. Air-drying may not be appropriate for the analysis of the more volatile organochlorine pesticides (e.g., the BHCs) or the more volatile of the semivolatile organics because of losses during the drying process. The use of sodium sulfate as a drying agent can lead to clogging of the frits in the cell with recrystallized sodium sulfate. (See “Caution” following Sec. 5.5.6.)

7.1.2 Waste samples - Multiphase waste samples must be prepared by the phase separation method in Chapter Two before extraction. This extraction procedure is for solids only.

7.1.3 Dry sediment/soil and dry waste samples amenable to grinding. Grind or otherwise reduce the particle size of the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Disassemble grinder between samples, according to manufacturer's instructions, and decontaminate with soap and water, followed by acetone and hexane rinses.

NOTE: The note in Sec. 7.1.1 also applies to the grinding process.

7.1.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The analyst may add anhydrous sodium sulfate, pelletized diatomaceous earth, sand, or other clean, dry reagents to the sample to make it more amenable to grinding.

7.2 Determination of percent dry weight - When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

7.2.1 Immediately after weighing the sample for extraction, weigh 5 - 10 g of the sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Grind a sufficient weight of the dried sample from Sec. 7.1 to yield the sample weight needed for the determinative method (usually 10 - 30 g). Grind the sample until it passes through a 10 mesh sieve.

7.4 Transfer the ground sample to an extraction cell of the appropriate size for the aliquot. Generally, an 11-mL cell will hold about 10 g of material, a 22-mL cell will hold about 20 g of material, and a 33-mL cell will hold about 30 g of material. The weight of a specific sample that a cell will contain depends on the bulk density of the sample and the amount of drying agent that must be added to the sample in order to make it suitable for extraction. Analysts should ensure that the sample aliquot extracted is large enough to provide the necessary sensitivity and choose the extraction cell size accordingly. Use disposable cellulose or glass fiber filters in the cell outlets. Clean sand may be used to fill any void volume in the extraction cells.

7.5 Add the surrogates listed in the determinative method to each sample. Add the matrix spike/matrix spike duplicate compounds listed in the determinative method to the two additional aliquots of the sample selected for spiking.

7.6 Place the extraction cell into the instrument or autosampler tray, as described by the instrument manufacturer.

7.7 Place a precleaned collection vessel in the instrument for each sample, as described by the instrument manufacturer. The total volume of the collected extract will depend on the specific instrumentation and the extraction procedure recommended by the manufacturer and may range from 0.5 to 1.4 times the volume of the extraction cell. Ensure that the collection vessel is sufficiently large to hold the extract.

7.8 Recommended extraction conditions

Oven temperature:	100°C
Pressure:	1500 - 2000 psi
Static time:	5 min (after 5 min pre-heat equilibration)
Flush volume:	60% of the cell volume
Nitrogen purge:	60 sec at 150 psi (purge time may be extended for larger cells)
Static Cycles:	1

7.8.1 Optimize the conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500 - 2000 psi should suffice.

7.8.2 Once established, the same pressure should be used for all samples extracted for the same analysis type.

7.9 Begin the extraction according to the manufacturer's instructions.

7.10 Collect each extract in a clean vial (see Sec. 7.7). Allow the extracts to cool after the extractions are complete.

7.11 The extract is now ready for concentration, cleanup, or analysis, depending on the extent of interferants and the determinative method to be employed. Refer to Method 3600 for guidance on selecting appropriate cleanup methods. Excess water present in extracts may be removed by filtering the extract through a bed of anhydrous sodium sulfate. Certain cleanup and/or determinative methods may require a solvent exchange prior to cleanup and/or sample analysis.

7.12 If the phosphoric acid solution in Sec. 5.5.5 is used for the extraction of chlorinated herbicides, then the extractor should be rinsed by pumping acetone through all the lines of the system. The use of other solvents for these analytes may not require this rinse step.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for guidance on quality control procedures. Refer to Method 3500 for specific guidance on extraction and sample preparation procedures.

8.2 Before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a solid matrix method blank (e.g., clean sand). Each time samples are extracted, and when there is a change in reagents, a method blank needs to be extracted and analyzed for the compounds of interest. The method blank should be carried through all stages of the sample preparation and measurement.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling procedures. A matrix spike/matrix spike duplicate, or matrix spike and duplicate sample analysis, and a laboratory control sample should be prepared and analyzed with each batch of samples prepared by this procedure, unless the determinative method provides other guidance.

8.4 Surrogate standards should be added to all samples when listed in the appropriate determinative method.

9.0 METHOD PERFORMANCE

9.1 Chlorinated pesticides and semivolatile organics

Single-laboratory accuracy data were obtained for chlorinated pesticides and semivolatile organics at three different spiking concentrations in three different soil types. Spiking concentrations ranged from 5 to 250 µg/kg for the chlorinated pesticides and from 250 to 12500 µg/kg for the semivolatiles. Spiked samples were extracted both by the Dionex Accelerated Solvent Extraction system and by a Perstorp Environmental Soxtec™ (automated Soxhlet). Extracts were analyzed either by Method 8270 or Method 8081. Method blanks, spikes and spike duplicates were included for the low concentration spikes; matrix spikes were included for all other concentrations. The data are reported in detail in Reference 1, and represent seven replicate extractions and analyses for each sample. Data summary tables are included in Methods 8270 and 8081.

9.2 Organophosphorus pesticides and chlorinated herbicides

Single-laboratory accuracy data were obtained for organophosphorus pesticides (OPPs) and chlorinated herbicides at two different spiking concentrations in three different soil types. Spiking concentrations ranged from 250 to 2500 µg/kg for the OPPs and from 50 to 5000 µg/kg for the chlorinated herbicides. Chlorinated herbicides were spiked with a mixture of the free acid and the ester (1:1). Spiked samples were extracted both by the Dionex Accelerated Solvent Extractor and by Soxhlet for the OPPs. Extracts were analyzed by Method 8141. Spiked chlorinated herbicides were extracted by the Dionex Accelerated Solvent Extractor and by the shaking method described in Method 8151. Extracts were analyzed by Method 8151. Method blanks, spikes and spike duplicates were included for the low concentration spikes; matrix spikes were included for all other concentrations. The data are reported in detail in Reference 2, and represent seven replicate extractions and analyses for each sample. Data summary tables are included in Methods 8141 and 8151.

9.3 PCBs

Single-laboratory accuracy data were obtained for PCBs from a soil sample with PCB content certified by NIST (Standard Reference Material, SRM 1939, River Sediment). A PCB-contaminated soil was purchased from a commercial source. Spiking or certified concentrations ranged from 1 to 1400 µg/kg. Samples were extracted by the Dionex Accelerated Solvent Extractor and by Soxtec™ (Perstorp Environmental). Extracts were analyzed using Method 8082. Method blanks, spikes and spike duplicates were included. The data are reported in Reference 2, and represent seven replicate extractions and analyses for each sample. Data summary tables are included in Method 8082.

10.0 REFERENCES

1. B. Richter, Ezzell, J., and Felix, D., "Single Laboratory Method Validation Report. Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) BNAs and Pesticides using Accelerated Solvent Extraction (ASE) with Analytical Validation by GC/MS and GC/ECD"; Document 116064.A, Dionex Corporation, June 16, 1994.

2. B. Richter, Ezzell, J., and Felix, D., "Single Laboratory Method Validation Report. Extraction of TCL/PPL (Target Compound List/Priority Pollutant List) OPPs, Chlorinated Herbicides and PCBs using Accelerated Solvent Extraction (ASE)". Document 101124, Dionex Corporation, December 2, 1994).

11.0 SAFETY

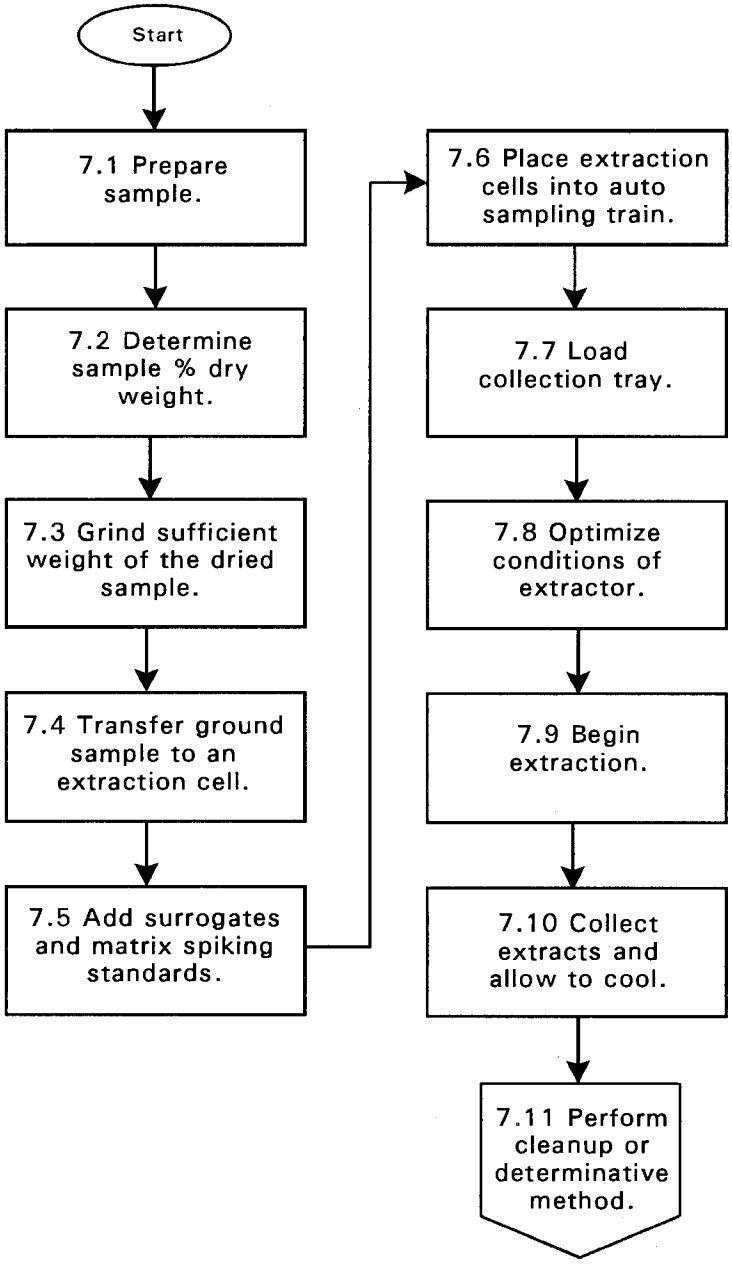
The use of organic solvents, elevated temperatures, and high pressures in Method 3545 present potential safety concerns in the laboratory. Common sense laboratory practices can be employed to minimize these concerns. However, the following sections describe additional steps that should be taken.

11.1 Extraction cells in the oven are hot enough to burn unprotected skin. Allow the cells to cool before removing them from the oven or use appropriate protective equipment (e.g., insulated gloves or tongs), as recommended by the manufacturer.

11.2 During the gas purge step, some solvent vapors may exit through a vent port in the instrument. Follow the manufacturer's directions regarding connecting this port to a fume hood or other means to prevent release of solvent vapors to the laboratory atmosphere.

11.3 The instrument may contain flammable vapor sensors and should be operated with all covers in place and doors closed to ensure proper operation of the sensors. If so equipped, follow the manufacturer's directions regarding replacement of extraction cell seals when frequent vapor leaks are detected.

PRESSURIZED FLUID EXTRACTION (PFE)



METHOD 3550B

ULTRASONIC EXTRACTION

See Disclaimer. See manufacturer's specifications for operational settings.

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of less than or equal to 20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of greater than 20 mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Chapter Four (Cleanup), Sec. 4.2.2, for applicable methods.

1.4 Ultrasonic extraction is not as rigorous as other extraction methods for soils/solids. Therefore, it is critical that the method (including the manufacturer's instructions) be followed explicitly in order to achieve the maximum extraction efficiency. See Sec. 7.0 for the critical aspects of the extraction procedure.

1.5 EPA has not validated Method 3550 for the extraction of organophosphorous compounds from solid matrices. In addition, there are concerns that the ultrasonic energy may lead to breakdown of some organophosphorous compounds (see Reference 3). As a result, this extraction technique should not be used for organophosphorous compounds without extensive validation on real-world samples. Such studies should assess the precision, accuracy, ruggedness, and sensitivity of the technique relative to the appropriate regulatory limits or project-specific concentrations of interest.

1.6 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.7 This method is not appropriate for applications where high extraction efficiencies of analytes at very low concentrations is necessary (e.g., demonstration of effectiveness of corrective action).

2.0 SUMMARY OF METHOD

2.1 Low concentration method - A 30-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 Medium/high concentration method - A 2-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using ultrasonic extraction. A portion of the extract is removed for cleanup and/or analysis.

3.0 INTERFERENCES

Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples.

4.2 Ultrasonic preparation - A horn-type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

4.2.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low and medium/high concentration.

4.2.2 Use a 3/4" horn for the low concentration method and a 1/8" tapered microtip attached to a 1/2" horn for the medium/high concentration method.

4.3 Sonabox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent dry weight.

4.4.1 Drying oven - capable of maintaining 105°C.

4.4.2 Desiccator.

4.4.3 Crucibles - Porcelain or disposable aluminum.

4.5 Pasteur glass pipets - 1-mL, disposable.

4.6 Beakers - 400-mL.

4.7 Vacuum or pressure filtration apparatus.

4.7.1 Buchner funnel.

4.7.2 Filter paper - Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus.

4.8.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.8.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.8.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.9 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.10 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.11 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The batch should be used in a hood.

4.12 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.

4.13 Vials - 2-mL, for GC autosampler, with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

4.15 Spatula - Stainless steel or PTFE.

4.16 Drying column - 20-mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.17 Syringe - 5-mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise specified, it is intended that all inorganic reagents shall conform to the specifications of the Committee on

Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents

Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix. Table 1 provides recovery data for selected semivolatile organic compounds extracted from an NIST SRM. The following sections provide guidance on the choice of solvents for various classes of analytes. All solvents must be pesticide quality or equivalent.

5.4.1 Semivolatile organics may be extracted with acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2 or acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}.

5.4.2 Organochlorine pesticides may be extracted with acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14} or acetone/methylene chloride (1:1,v/v), CH_3COCH_3/CH_2Cl_2.

5.4.3 PCBs may be extracted with acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}, acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2 or hexane, C_6H_{14}.

5.4.4 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest in the sample matrix (see Method 3500, Sec. 8.0).

5.5 Exchange solvents - All solvents must be pesticide quality or equivalent.

5.5.1 Hexane, C_6H_{14}.

5.5.2 2-Propanol, $(CH_3)_2CHOH$.

5.5.3 Cyclohexane, C_6H_{12}.

5.5.4 Acetonitrile, CH_3CN.

5.5.5 Methanol, CH_3OH.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

As noted in Sec. 1.4, ultrasonic extraction is not as rigorous a method as other extraction methods for soils/solids. Therefore, it is critical that the method be followed explicitly (including the manufacturer's instructions) to achieve the maximum extraction efficiency. At a minimum, successful use of this technique requires that:

- The extraction device must have a minimum of 300 watts of power and be equipped with appropriate size disrupter horns (see Sec. 4.2).

- The horn must be properly maintained, including tuning according to the manufacturer's instructions prior to use, and inspection of the horn tip for excessive wear.

- The samples must be properly prepared by thorough mixing with sodium sulfate so that it forms a free-flowing powder prior to the addition of the solvent.

- The extraction horns used for the low concentration and high concentration protocols (Sec. 7.3 and Sec. 7.4, respectively) are not interchangeable. Results indicate that the use of the 3/4" horn is inappropriate for the high concentration method, particularly for extraction of very non-polar organic compounds such as PCBs, which are strongly adsorbed to the soil matrix.

- Three extractions are performed with the appropriate solvent, the extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.

- Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. The analyst must observe such mixing at some point during the extraction process.

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiple phases must be prepared by the phase separation method in Chapter Two before extraction. This extraction procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.1.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of anhydrous sodium sulfate to the sample (1:1) may make the mixture amenable to grinding.

7.2 Determination of percent dry weight - When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Extraction method for samples expected to contain low concentrations of organics and pesticides (less than or equal to 20 mg/kg):

7.3.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

7.3.1.1 Weigh approximately 30 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g.

7.3.1.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

7.3.1.3 Add 1.0 mL of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks. Consult Method 3500, Secs. 5.0 and 8.0 for guidance on the appropriate choice of surrogate compounds and concentrations.

7.3.1.4 For the sample in each batch selected for spiking, add 1.0 mL of the matrix spiking solution. Consult Method 3500, Secs. 5.0 and 8.0 for guidance on the appropriate choice of matrix spiking compounds and concentrations.

7.3.1.5 If gel permeation cleanup (Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column.

7.3.1.6 Immediately add 100 mL of the appropriate/recommended extraction solvent or solvent mixture (see Sec. 5.4 and Table 1).

7.3.2 Place the bottom surface of the tip of the #207 (or equivalent) 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.

NOTE: Be sure the horn is properly tuned according to the manufacturer's instructions.

7.3.3 Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Do not use microtip probe.

7.3.4 Decant the extract and filter it through Whatman No. 41 filter paper (or equivalent) in a Buchner funnel that is attached to a clean 500-mL filtration flask. Alternatively, decant the extract into a centrifuge bottle and centrifuge at low speed to remove particles.

7.3.5 Repeat the extraction two or more times with two additional 100 mL portions of solvent. Decant off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample into the Buchner funnel and rinse with extraction solvent. Apply a vacuum to the filtration flask, and collect the solvent extract. Continue filtration until all visible solvent is removed from the funnel, but do not attempt to completely dry the sample, as the continued application of a vacuum may result in the loss of some analytes. Alternatively, if centrifugation is used in Sec. 7.3.4, transfer the entire sample to the centrifuge bottle. Centrifuge at low speed, and then decant the solvent from the bottle.

7.3.6 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the Kuderna-Danish apparatus following manufacturer's instructions. Transfer filtered extract to a 500-mL evaporator flask and proceed to the next section.

7.3.7 Add one to two clean boiling chips to the evaporation flask, and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 - 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 - 15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.8 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Sec. 7.3.10, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1 - 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.3.10 or adjusted to 10.0 mL with the solvent last used.

7.3.10 If further concentration is indicated in Table 1, either micro Snyder column technique (Sec. 7.3.10.1) or nitrogen blowdown technique (Sec. 7.3.10.2) may be used to adjust the extract to the final volume required.

7.3.10.1 Micro Snyder column technique

7.3.10.1.1 Add a clean boiling chip and attach a two-ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the

water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the liquid reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint with approximately 0.2 mL of appropriate solvent and add to the concentrator tube. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.3.10.2 Nitrogen blowdown technique

7.3.10.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample, since it may introduce contaminants.

7.3.10.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.4 Extraction method for samples expected to contain high concentrations of organics (greater than 20 mg/kg):

7.4.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.4.2 Add 2 g of anhydrous sodium sulfate to sample in the 20-mL vial and mix well.

7.4.3 Surrogates are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate spiking solution and on the matrix spike solution).

7.4.3.1 Add 1.0 mL of surrogate spiking solution to sample mixture.

7.4.3.2 For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard.

7.4.3.3 If gel permeation cleanup (Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column.

7.4.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8 in. tapered microtip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%. Extraction solvents are:

7.4.4.1 For nonpolar compounds (i.e., organochlorine pesticides and PCBs), use hexane or appropriate solvent.

7.4.4.2 For other semivolatile organics, use methylene chloride.

7.4.5 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the sample extract through the glass wool and collect the extract in a suitable container. The entire 10 mL of extraction solvent cannot be recovered from the sample. Therefore, the analyst should collect a volume appropriate for the sensitivity of the determinative method. For instance, for methods that do not require that the extract be concentrated further (e.g., Method 8081 typically employs a final extract volume of 10 mL), the extract may be collected in a scintillation vial or other sealable container. For extracts that will require further concentration, it is advisable to collect a standard volume for all such samples in order to simplify the calculation of the final sample results. For instance, collect 5.0 mL of extract in a clean concentrator tube. This volume represents exactly half of the total volume of the original sample extract. As necessary, account for the "loss" of half of the extract in the final sample calculations, or concentrate the final extract to one-half the nominal final volume (e.g., 0.5 mL vs. 1.0 mL) to compensate for the loss.

7.4.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

7.5 If analysis of the extract will not be performed immediately, stopper the concentrator tube and refrigerate. If the extract will be stored longer than 2 days, it should be transferred to a vial with a PTFE-lined cap and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spike, and replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.

2. Christopher S. Hein, Paul J. Marsden, Arthur S. Shurtleff, "Evaluation of Methods 3540 (Soxhlet) and 3550 (Sonication) for Evaluation of Appendix IX Analytes from Solid Samples", S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October 1988.

3. Kotronarou, A., et al., “Decomposition of Parathion in Aqueous Solution by Ultrasonic Irradiation,” *ES&T*, 1992, Vol. 26, 1460-1462.

TABLE 1
EFFICIENCIES OF VARIOUS EXTRACTION SOLVENT SYSTEMS[a]

Compound	CAS No.[b]	ABN[c]	Solvent System[d] A %R	A SD	B %R	B SD	C %R	C SD	D %R	D SD	E %R	E SD
4-Bromophenyl phenyl ether	101-55-3	N	64.2	6.5	56.4	0.5	86.7	1.9	84.5	0.4	73.4	1.0
4-Chloro-3-methylphenol	59-50-7	A	66.7	6.4	74.3	2.8	97.4	3.4	89.4	3.8	84.1	1.6
Bis(2-chloroethoxy)methane	111-91-1	N	71.2	4.5	58.3	5.4	69.3	2.4	74.8	4.3	37.5	5.8
Bis(2-chloroethyl) ether	111-44-4	N	42.0	4.8	17.2	3.1	41.2	8.4	61.3	11.7	4.8	1.0
2-Chloronaphthalene	91-58-7	N	86.4	8.8	78.9	3.2	100.8	3.2	83.0	4.6	57.0	2.2
4-Chlorophenyl phenyl ether	7005-72-3	N	68.2	8.1	63.0	2.5	96.6	2.5	80.7	1.0	67.8	1.0
1,2-Dichlorobenzene	95-50-1	N	33.3	4.5	15.8	2.0	27.8	6.5	53.2	10.1	2.0	1.2
1,3-Dichlorobenzene	541-73-1	N	29.3	4.8	12.7	1.7	20.5	6.2	46.8	10.5	0.6	0.6
Diethyl phthalate	84-66-2	N	24.8	1.6	23.3	0.3	121.1	3.3	99.0	4.5	94.8	2.9
4,6-Dinitro-*o*-cresol	534-52-1	A	66.1	8.0	63.8	2.5	74.2	3.5	55.2	5.6	63.4	2.0
2,4-Dinitrotoluene	121-14-2	N	68.9	1.6	65.6	4.9	85.6	1.7	68.4	3.0	64.9	2.3
2,6-Dinitrotoluene	606-20-2	N	70.0	7.6	68.3	0.7	88.3	4.0	65.2	2.0	59.8	0.8
Heptachlor epoxide	1024-57-3	N	65.5	7.8	58.7	1.0	86.7	1.0	84.8	2.5	77.0	0.7
Hexachlorobenzene	118-74-1	N	62.1	8.8	56.5	1.2	95.8	2.5	89.3	1.2	78.1	4.4
Hexachlorobutadiene	87-68-3	N	55.8	8.3	41.0	2.7	63.4	4.1	76.9	8.4	12.5	4.6
Hexachlorocyclopentadiene	77-47-4	N	26.8	3.3	19.3	1.8	35.5	6.5	46.6	4.7	9.2	1.7
Hexachloroethane	67-72-1	N	28.4	3.8	15.5	1.6	31.1	7.4	57.9	10.4	1.4	1.2
5-Nitro-*o*-toluidine	99-55-8	B	52.6	26.7	64.6	4.7	74.7	4.7	27.9	4.0	34.0	4.0
Nitrobenzene	98-95-3	N	59.8	7.0	38.7	5.5	46.9	6.3	60.6	6.3	13.6	3.2
Phenol	108-95-2	A	51.6	2.4	52.0	3.3	65.6	3.4	65.5	2.1	50.0	8.1
1,2,4-Trichlorobenzene	120-82-1	N	66.7	5.5	49.9	4.0	73.4	3.6	84.0	7.0	20.0	3.2

[a] Percent recovery of analytes spiked at 200 mg/kg into NIST sediment SRM 1645
[b] Chemical Abstracts Service Registry Number
[c] Compound Type: A = Acid, B = Base, N = neutral
[d] Solvent system A = Methylene chloride
Solvent system B = Methylene chloride/Acetone (1/1)
Solvent system C = Hexane/Acetone (1/1)
Solvent system D = Methyl t-butyl ether
Solvent system E = Methyl t-butyl ether/Methanol (2/1)

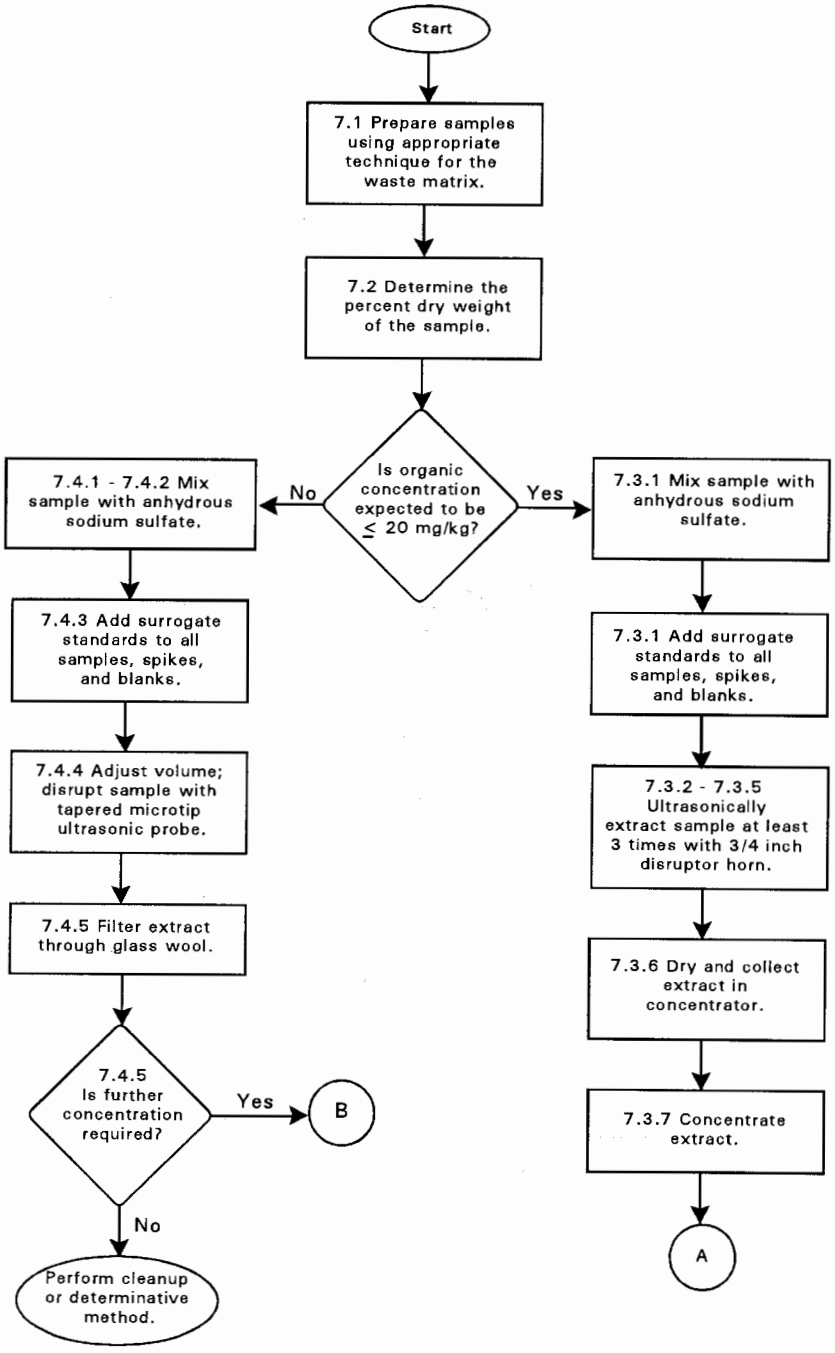
TABLE 2
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

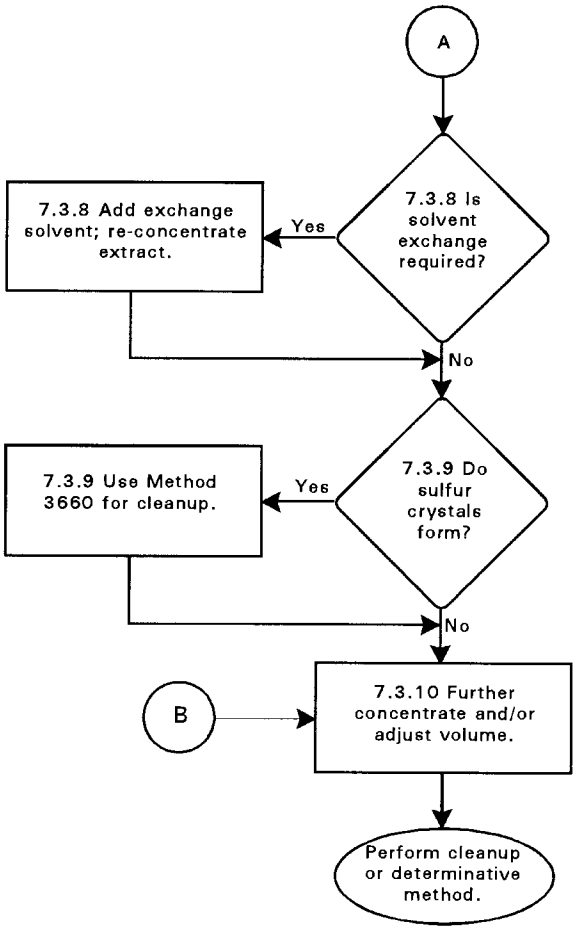
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	as received	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8091	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8111	as received	hexane	hexane	2.0	10.0
8121	as received	hexane	hexane	2.0	1.0
8141	as received	hexane	hexane	10.0	10.0
8270[c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0
8321	as received	methanol	-	-	1.0
8325	as received	methanol	-	-	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

[b] Phenols may be analyzed by Method 8041, using a 1.0-mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5-mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.


Start
7.1 Prepare samples using appropriate technique for the waste matrix.
7.2 Determine the percent dry weight of the sample.
Is organic concentration expected to be ≤ 20 mg/kg?
No
Yes
7.4.1 - 7.4.2 Mix sample with anhydrous sodium sulfate.
7.4.3 Add surrogate standards to all samples, spikes, and blanks.
7.4.4 Adjust volume; disrupt sample with tapered microtip ultrasonic probe.
7.4.5 Filter extract through glass wool.
7.4.5 Is further concentration required?
Yes
B
No
Perform cleanup or determinative method.
7.3.1 Mix sample with anhydrous sodium sulfate.
7.3.1 Add surrogate standards to all samples, spikes, and blanks.
7.3.2 - 7.3.5 Ultrasonically extract sample at least 3 times with 3/4 inch disruptor horn.
7.3.6 Dry and collect extract in concentrator.
7.3.7 Concentrate extract.
A


A
7.3.8 Is solvent exchange required?
Yes
7.3.8 Add exchange solvent; re-concentrate extract.
No
7.3.9 Do sulfur crystals form?
Yes
7.3.9 Use Method 3660 for cleanup.
No
B
7.3.10 Further concentrate and/or adjust volume.
Perform cleanup or determinative method.

METHOD 3560

SUPERCRITICAL FLUID EXTRACTION OF TOTAL RECOVERABLE PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 3560 describes the use of supercritical fluids for the extraction of total recoverable petroleum hydrocarbons (TRPHs) from soils, sediments, fly ash, solid-phase extraction media, and other solid materials which are amenable to extraction with conventional solvents. This method is suitable for use with any supercritical fluid extraction (SFE) system that allows extraction conditions (e.g., pressure, temperature, flow rate) to be adjusted to achieve separation of the TRPHs from the matrices of concern.

1.2 Method 3560 is not suitable for the extraction of low-boiling TRPHs such as gasoline.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A known amount of sample is transferred to the extraction vessel. The sample is then extracted in the dynamic mode for up to 30 min with supercritical carbon dioxide at 340 atm, 80°C and a gas flow rate of 500 - 1000 mL/min.

2.2 After depressurization of the carbon dioxide, the extracted TRPHs are collected in a small volume of tetrachloroethene, methylene, isooctane, or other solvent appropriate for the determinative method (see Sec. 5.4), or on a sorbent material, depending on the SFE system used. In the latter case, the analytes are collected by rinsing the sorbent material with a solvent appropriate for the determinative method.

2.3 After collection, the TRPHs are analyzed by the appropriate determinative method.

3.0 INTERFERENCES

3.1 The analyst must demonstrate through the analysis of reagent blanks (collection solvent treated as per Sec. 7.4) that the supercritical fluid extraction system is free from interferants. To do this, perform a simulated extraction using an empty extraction vessel and a known amount of carbon dioxide under the same conditions as those used for sample extraction, and determine the background contamination by analyzing the extract by the appropriate determinative method (e.g., Methods 8015 or 8440). If glass wool and a drying agent are used with the sample, these materials should be included when performing a reagent blank check.

3.2 The extraction vessel(s), the frits, the restrictor(s), and the multi-port valve may retain solutes whenever high-concentration samples are extracted. It is, therefore, good practice to clean the extraction system after each extraction. Replacement of the restrictor may be necessary when reagent blanks indicate carryover. At least one reagent blank should be prepared and analyzed daily when the instrument is in use. Furthermore, reagent blanks should be prepared and analyzed after each extraction of a high-concentration sample (concentration in the high ppm range). If reagent

blanks continue to indicate contamination, even after replacement of the extraction vessel and the restrictor, the multi-port valve must be cleaned.

4.0 APPARATUS AND MATERIALS

4.1 Supercritical fluid extractor and associated hardware.

WARNING: A safety feature to prevent overpressurization is required on the extractor. This feature should be designed to protect the laboratory personnel and the instrument from possible injuries or damage resulting from equipment failure under high pressure.

4.1.2 Extraction vessel - Stainless-steel vessel with end fittings and 0.5-or 2-µm frits. Use the extraction vessel supplied by the manufacturer of the SFE system being used. The PEEK (polyether ether ketone) extraction vessels supplied by Isco, Inc. are acceptable for use with the Isco SFE system.

Fittings used for the extraction vessel must be capable of withstanding the required extraction pressures. The maximum operating pressure for most extractors is 500 atm. However, extractors with higher pressure ratings are available. Check with the manufacturer of the particular extraction system on the maximum operating pressure and temperature for that system. Make sure that the extraction vessels are rated for such pressures and temperatures.

4.1.3 Restrictor - 50 µm ID x 150 or 375 µm OD x 25 to 60 cm length piece of uncoated fused-silica tubing (J&W Scientific or equivalent). Other restrictors may be used, including tapered restrictors, static pinhole restrictors, frit restrictors, or variable orifice restrictors (either manual or computer-controlled), crimped metal tubing, or polyether ether ketone (PEEK) tubing. Check with the manufacturer of the SFE system on the advantages and disadvantages of the various restrictor designs.

4.1.4 Collection device - The extracted TRPHs can be collected either in vials containing solvent, or they can be trapped on a sorbent material (e.g., octadecyl-bonded silica, stainless steel beads).

4.1.4.1 When the analytes are collected in solvent, install the restrictor through a hole made through the cap and septum of the vial, and position the restrictor end about 0.5 inch from the bottom of the vial. A syringe needle should also be inserted through the septum of the vial (with the tip positioned just below the septum) to prevent buildup of pressure in the vial. Use the type of vials appropriate for the SFE system used.

4.1.4.2 When the analytes are trapped on a sorbent material, it is important to ensure that breakthrough of the analytes from the trap does not occur. Desorption from the trapping medium can be accomplished by increasing the temperature of the trap and using a solvent to remove the analytes. Use the conditions suggested by the manufacturer of the particular system to recover the analytes.

4.2 Carbon dioxide cylinder balance (optional) - Balances from White Associates, Catalog No. 30, Scott Specialty Gases Model 5588D, or equivalent, can be used to monitor the fluid usage. Such a device is useful because carbon dioxide tanks used for SFE are not equipped with regulators.

This makes it difficult to determine when the tank needs to be replaced. The monitoring of carbon dioxide usage is optional and, if performed, may be accomplished by a variety of other means.

4.3 Tools required include: screwdriver (flat-blade), adjustable wrench, pliers, tubing cutter, and various small open-end wrenches for small fittings.

4.4 Magnesium sulfate monohydrate - may be used as received.

4.5 Silanized glass wool - requires high-temperature treatment (bake in a muffle furnace at 400°C for 2 to 4 hours) prior to use to remove any petroleum hydrocarbons.

5.0 REAGENTS

5.1 Carbon dioxide, CO_2 - Either supercritical fluid chromatography (SFC)- or SFE-grade CO_2 may be acceptable for use in SFE. However, SFC-grade CO_2 may contain more impurities than SFE-grade, and therefore may be unsuitable for trace analysis. Aluminum cylinders are generally preferred over steel cylinders. Depending on the specific instrumentation, the cylinders may need to be fitted with eductor tubes and the contents pressurized under 1500 psi of helium head pressure. Consult the SFE system manufacturer's instructions regarding the specific cylinder configuration required.

5.2 Carbon dioxide (CO_2) for cryogenic cooling - Certain parts of some models of extractors (i.e., the high-pressure pump head and the analyte trap) must be cooled during use. The carbon dioxide used for this purpose must be dry (< 50 ppm water content), and it must be supplied in tanks with a full-length eductor tube.

5.3 Tetrachloroethene, C_2Cl_4 (spectrophotometric grade) - Used for the collection of TRPHs for determination by IR. Analyze a reagent blank to ensure no interferences are present at the TRPH wavelengths. Chlorofluorocarbons are not suitable for use with this method because of risk to the ozone layer.

5.4 Other pesticide-quality solvents may be used for the collection of TRPHs when these analytes are not determined by IR. The choice of solvent should be based on the determinative technique to be employed. For GC methods, methylene chloride or isooctane may be appropriate solvents. Because of concerns about stratospheric ozone depletion, chlorofluorocarbons (CFCs) are not appropriate solvents.

5.5 Copper filings - Copper filings added to remove elemental sulfur must have a shiny bright appearance to be effective. To remove oxides, treat with dilute nitric acid, rinse with reagent water to remove all traces of acid, rinse with acetone (copper will darken if acid is still present), and dry under a stream of nitrogen.

5.6 Drying agents - Anhydrous magnesium sulfate or diatomaceous earth.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Solid samples should be collected and stored as any other solid samples containing semivolatile organics.

6.2 See Chapter Four for guidance relating to semivolatile organics (including holding times).

7.0 PROCEDURE

7.1 Determination of sample % dry weight - In certain cases, sample results are desired based on a dry-weight basis. When such data are desired, a separate portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or should be vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

Immediately after weighing the sample for extraction, weigh an additional 5 - 10 g of the remaining sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.2 Safety considerations - Read Sec. 11.0, "Safety", before attempting to perform this procedure.

7.3 Sample handling

7.3.1 Decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves and rocks.

7.3.2 Weigh 3 g of sample into a precleaned aluminum dish. A drying agent (e.g., anhydrous magnesium sulfate or diatomaceous earth) may be added to samples that contain water in excess of 20% to increase porosity or to bind water. Alternatively, magnesium sulfate monohydrate is an excellent drying agent, and the amount of heat released (compared to anhydrous magnesium sulfate) is small, thereby minimizing the loss of volatile petroleum hydrocarbons. The amount of the drying agent will depend on the water content of the sample. Typically, a ratio of 1:1 works well for wet soils and sediment materials. However, a certain amount of water (up to 20 percent) in the sample has been shown to improve recoveries from certain matrices; therefore, if the sample is dry, water may optionally be added to bring the moisture content to approximately 20 percent.

7.3.2.1 If drying agent has been added to the sample, store the mixture of sample and drying agent for several hours (preferably overnight) at 4°C, with a minimum of headspace. This additional storage time is necessary to achieve acceptable analyte recovery. This step is not necessary if the alternate conditions described in Sec. 7.4.2.1 are used.

7.3.3 Transfer the weighed sample to a clean extraction vessel. The volume of the extraction vessel should match the sample volume. Use two plugs of silanized glass wool to hold the sample in place and fill the void volume (alternatively, drying agent or clean sand can be used to fill the void volume). Attach the end fittings, and install the extraction vessel in the oven. Always use clean frits for each extraction vessel.

7.4 Sample extraction

7.4.1 Fill the collection vessel with 3 mL of tetrachloroethene or other appropriate collection solvent. Chlorofluorocarbons are not suitable for use with this method because of risk to the ozone layer.

7.4.2 Set the pressure at 340 atm and the temperature at 80°C. Follow the manufacturer's instructions in setting up the instrument. Extract for 30 minutes in the dynamic mode. Note the safety precautions in Sec. 11.0 on venting the instrument into a chemical fume hood.

7.4.2.1 Alternatively, extract with a pressure greater than or equal to 340 atm at 150°C for 25 minutes, and a gas flow rate of 3500 to 4000 mL/min. These parameters dry the sample during the extraction, thus extended drying is not necessary for wet samples (Sec. 7.3.2.1).

7.4.2.2 A sorbent trap maintained above 0°C may be necessary for effective analyte trapping. The restrictor should resist plugging by water, since water released from the sample may pass through the restrictor.

7.4.3 After the extraction time has elapsed, the system should automatically switch to the equilibrate mode. At this point, remove the collection vessel(s) containing the extract. Since the depressurization of the carbon dioxide at the end of the restrictor outlet results in a gas flowrate of about 500 to 1000 mL/min, part of the collection solvent will evaporate during the extraction. However, cooling caused by the rapid expansion of the carbon dioxide limits the loss of solvent, so that approximately 2 mL remains (when tetrachloroethene is used) after a 30 min extraction. To prevent the collection solvent from freezing, place the collection vial in a beaker with warm water (approximately 25°C). The extract is then brought to the desired volume, or concentrated further. See Method 3510 for concentration techniques by micro Kuderna-Danish or nitrogen blowdown. Concentration must be performed in a chemical fume hood to prevent contamination of the laboratory environment.

7.4.4 The extract is ready for analysis by Method 8015, Nonhalogenated Volatile Organics by Gas Chromatography, or Method 8440, Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry.

7.5 SFE System Maintenance

7.5.1 Depressurize the system following the manufacturer's instructions.

7.5.2 After extraction of an especially tarry sample, the frits may require replacement to ensure adequate extraction fluid flow through the restrictor. In addition, very fine particles contained in samples can clog the frits necessitating replacement.

7.5.3 Clean the extraction vessel after each sample. The cleaning procedure depends on the type of sample. After removing the bulk of the extracted sample from the extraction vessel, the cell should be scrubbed with an ionic detergent, water, and a bottle brush. After extraction of tarry materials, use solvent rinses or an ultrasonic bath to clean the extraction vessel.

7.5.4 For samples known to contain elemental sulfur, use copper filings to remove the dissolved sulfur from the fluid. The copper filings (1 to 2 g per sample) can be packed in a

separate extraction vessel connected to the outlet end of the sample extraction vessel, or they can be mixed with the sample, and a plug of copper filings can be loaded in the extraction vessel with the sample such that any sulfur extracted by the carbon dioxide can be removed before the stream of carbon dioxide containing the analytes reaches the restrictor.

7.5.5 The procedure to be followed in emptying the syringe pump depends upon the type of fluid being used. In the case of carbon dioxide, which is a gas at ambient temperature and pressure, it is only necessary to vent the gas to a fume hood by allowing it to expand across the purge valve. Follow the manufacturer's instructions in emptying the syringe pump.

7.5.6 To change fluid supply cylinders on a system with a syringe pump, it is necessary to empty the syringe pump as described in Sec. 7.5.5. Upon completion of the emptying procedure, the piston will be at its maximum extension, and the syringe pump outlet valve and purge valve will be open. Then proceed as follows:

7.5.6.1 Connect the new fluid supply cylinder to the syringe pump inlet line, and open the supply cylinder valve.

7.5.6.2 Open the pump inlet valve. The new fluid will flow through the inlet line to the syringe pump and out through the vent.

7.5.6.3 Close the syringe pump outlet valve and the vent/purge valve.

7.5.7 Restrictor removal and installation - Follow manufacturer's instructions. When using fused-silica restrictors, it may be necessary to replace the restrictor after each sample, especially when extracting samples contaminated with heavy oils.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures and to Method 3500 for sample preparation quality control procedures.

8.2 Each time samples are extracted, and when there is a change in reagents, a reagent blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. Any reagent blanks, matrix spike samples, or replicate samples should be subjected to exactly the same analytical procedures (Sec. 7.4) as those used on actual samples.

8.3 All instrument operating conditions and parameters must be recorded.

9.0 METHOD PERFORMANCE

9.1 Refer to Methods 8440 and 8015 for performance data.

9.2 Use standard reference materials to establish the performance of the method with contaminated samples.

10.0 REFERENCES

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2. Pyle, S.M., and M.M. Setty, "Supercritical Fluid Extraction of High-Sulfur Soils with Use of a Copper Scavenger", Talanta, 1991, 38 (10), 1125-1128.

3. Bruce, M.L., "Supercritical Fluid Extraction (SFE) of Total Petroleum Hydrocarbons (TPHs) with Analysis by Infrared Spectroscopy", Proceedings of the Eighth Annual Waste Testing and Quality Assurance Symposium, July, 1992.

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11.0 SAFETY

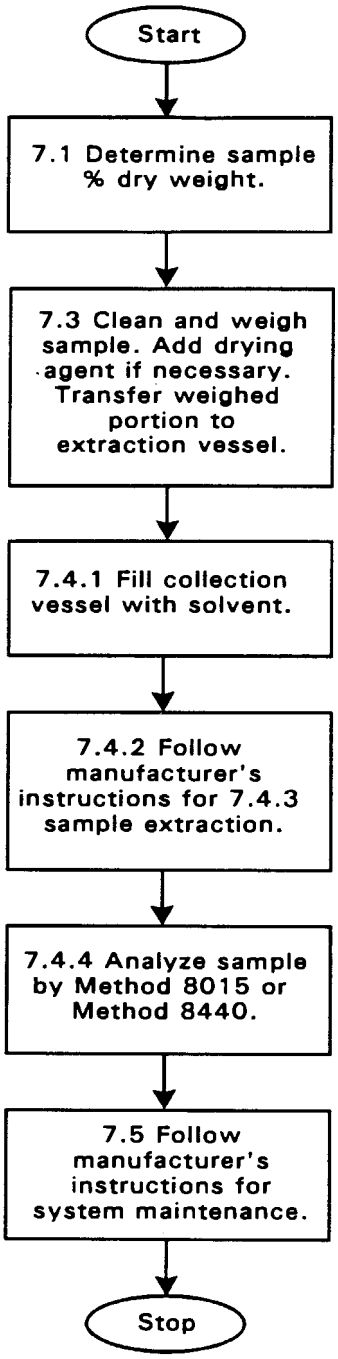
11.1 When liquid carbon dioxide comes in contact with skin, it can cause "burns" because of its low temperature (-78°C). Burns are especially severe when CO_2 is modified with organic liquids.

11.2 The extraction fluid, which may contain a modifier, usually exhausts through an exhaust gas and liquid waste port on the rear of the panel of the extractor. This port must be connected to a chemical fume hood to prevent contamination of the laboratory atmosphere.

11.3 Combining modifiers with supercritical fluids requires an understanding and evaluation of the potential chemical interaction between the modifier and the supercritical fluid, and between the supercritical fluid or modifier and the analyte(s) or matrix.

11.4 When carbon dioxide is used for cryogenic cooling, typical coolant consumption is 5 L/min, which results in a carbon dioxide level of 900 ppm for a room of 4.5 m x 3.0 m x 2.5 m, assuming 10 air exchanges per hour. The NIOSH time-weighted average (TWA) concentration is 9000 ppm (American Conference of Governmental Industrial Hygienists, 1991-1992).

SUPERCRITICAL FLUID EXTRACTION OF TOTAL RECOVERABLE PETROLEUM HYDROCARBONS



SUPERCRITICAL FLUID EXTRACTION OF POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 3561 describes the use of supercritical fluids for the extraction of polynuclear aromatic hydrocarbons (PAHs) from soils, sediments, fly ash, solid-phase extraction media, and other solid materials which are amenable to extraction with conventional solvents. This method is suitable for use with any supercritical fluid extraction (SFE) system that allows extraction conditions (e.g., pressure, temperature, flow rate) to be adjusted to achieve extraction of the PAHs from the matrices of concern. The following compounds may be determined by this method:

Compound	CAS No[a]
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benz(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(g,h,i)perylene	191-24-2
Benzo(a)pyrene	50-32-8
Chrysene	218-01-9
Dibenz(a,h)anthracene	53-70-3
Fluoranthene	206-44-0
Fluorene	86-73-7
Indeno(1,2,3-cd)pyrene	193-39-5
Naphthalene	91-20-3
Phenanthrene	85-01-8
Pyrene	129-00-0

[a] Chemical Abstract Service Registry Number

1.2 Method 3561 is not suitable for the extraction of PAHs from liquid samples without some treatment of the liquid prior to introduction into the SFE system. If liquid samples are not first "stabilized," the sample may be extruded through the end pieces of the SFE device without undergoing extraction. In the case of aqueous samples, one approach is to use solid-phase extraction (SPE), as described in Method 3535. The aqueous sample may be passed through an SPE disk and the analytes extracted from the disk using SFE.

1.3 The extraction conditions listed in this procedure (Sec. 7.5) were used to develop the data using a variable restrictor and solid trapping media referenced in Sec. 9.2. Other extraction conditions and equipment are acceptable as long as appropriate method performance is demonstrated. The method performance demonstration should be based on the extraction of a certified sample, not on spiked soil/solids. Alternatively, a comparison of SFE and Soxhlet extraction data using an environmentally contaminated PAH sample may be performed. Follow the guidance

for the initial demonstration of laboratory proficiency found in Section 8.0 of Method 3500, but utilize a weathered sample instead of a spiked sample.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The method is divided into three discrete steps. The extraction conditions for the first two steps are designed to ensure the best recovery for the range of volatilities found among the PAHs. The third step is used as a final sweep of modifier within the system. It should be noted that the separation of the PAHs into the two arbitrary classes of the "more volatile PAHs" (step 1) and the "lesser volatile PAHs" (step 2) is not a clean separation of compounds, but a rough group separation depending upon the actual compounds and their relative abundance in the sample matrix. The net sum of the two groups is recombined in the end and thus empirically does not depend upon a discrete definition or naming of the compounds in each group.

2.1.1 Step 1 - The more volatile PAHs are extracted and recovered in this step using pure CO_2 at moderately low density and temperature and with cold trapping on an ODS trap. These PAHs are reconstituted into an autosampler vial with 0.8 mL collected fraction volume.

2.1.2 Step 2 - The lesser volatile PAHs are removed in this step using a mixture of CO_2 with water and methanol as the extraction fluid, higher operating temperature and density in the extraction region, and a higher temperature in the trapping region with the ODS. The PAHs are not reconstituted directly after the second step.

2.1.3 Step 3 - A short third step with pure CO_2 (but with all other conditions as in the second step) is used to purge the system of modifier before depressurization. The analytes recovered in the second step (and possibly, any moved during the beginning of the third step) are reconstituted in the same autosampler vial containing the first fraction, using another 0.8-mL collected fraction volume. Therefore, all recovered analytes are merged automatically into a single fraction to be analyzed by HPLC.

2.2 There are also optional extraction solvents and SFE extraction conditions provided that are more amenable to GC and GC/MS analysis.

3.0 INTERFERENCES

3.1 The analyst must demonstrate through the analysis of reagent blanks (collection solvent treated as per Sec. 7.4) that the supercritical fluid extraction system is free from interferants. To do this, perform a simulated extraction using an empty extraction vessel and a known amount of carbon dioxide under the same conditions as those used for sample extraction, and determine the background contamination by analyzing the extract by the appropriate determinative method.

3.2 The extraction vessel(s), the end-frits, the nozzle [restrictor(s)], and the multi-port valve(s) may retain solutes whenever high-concentration samples are extracted. It is, therefore, good practice to clean the extraction system after such extractions. Replacement of suspected parts of the system should be done when reagent blanks indicate carryover. At least one reagent blank should be prepared and analyzed daily when the instrument is in use. Furthermore, reagent blanks should be prepared and analyzed after each extraction of a high-concentration sample (high part per

million or mg/kg range). If reagent blanks continue to indicate contamination, even after replacement of the extraction vessel (and the restrictor, if a fixed restrictor system is used), the multi-port valve must be cleaned. The operator must be ever vigilant against impurities arising from liquid solvents and carbon dioxide itself. Avoid any apparatus, valves, solenoids, and other hardware that contain lubricants, and chlorofluorohydrocarbon materials that can serve as background contaminant sources.

3.3 When using modifiers, it is important to consider that the modifiers at collection regions that are colder than the boiling point of the modifier(s) may cause some modifier condensation in that region. Depending upon the specific design of the instrumentation and the quantities of modifiers used within a step, there is a potential problem of flooding the collection region and thereby losing the analytes of interest. With SFE instrumentation employing solid (packed) traps for the collection and concentration of the extracted components, a convenient guideline is to think of the trap as a packed GC column during the extraction step (the CO_2 and any modifiers are the gaseous mobile phase) and as a packed LC column during the reconstitution step. Therefore, migration during the "GC-column-like" operation should be minimized by the selection of various parameters: trap temperature, chemical activity of the packing, expended flow rates, and extraction times (how long the migration has to proceed). Migration during the "LC-column-like" operation should be controlled to trade-off band-broadening with elution time through the use of reconstitution solvent flow rate and composition and the trap temperature during reconstitution.

3.4 Refer to Method 3500, Sec. 3.0, for general extraction interference guidance.

4.0 APPARATUS AND MATERIALS

4.1 Supercritical fluid extractor and associated hardware - Any supercritical fluid extraction system that can achieve the extraction conditions and performance specifications detailed in this procedure may be used.

Figure 1 depicts a typical supercritical fluid extractor system, including a carbon dioxide source, a pumping system (liquid carbon dioxide), an extraction thimble, a restriction device, and analyte collection device, temperature control systems for several zones, and an overall system controller. The lower left-hand side of Figure 1 depicts a cylinder of liquid carbon dioxide, which is the extractant fluid. The carbon dioxide is provided as a liquid-gas mixture. Because the liquid is the more dense of the two phases, it is drawn from the bottom of the tank with an eductor tube. It is essential that a full-length eductor tube is installed in the cylinder, regardless of the grade of carbon dioxide used. The carbon dioxide remains a liquid throughout the pumping or compression zones, and passes through small-diameter metal tubing as it approaches the extraction thimble. Some systems may include a preheating zone in front of the extraction zone, so that supercritical temperature, pressure, and density conditions are applied immediately to the analyte matrix in the thimble. Analytes are collected just beyond the exit end of the restrictor, either 1) on an impinged surface, such as a small, packed trap, or 2) in an empty vial or a vial containing an appropriate liquid.

WARNING: A safety feature to prevent over-pressurization is required on the extractor. This feature should be designed to protect the laboratory personnel and the instrument from possible injuries or damage resulting from equipment failure under high pressure.

4.1.1 Extraction vessel - Use the extraction vessel supplied by the manufacturer of the SFE system being used. The vessels may be constructed of stainless steel, polyether ether ketone (PEEK), or other suitable materials. Both the extraction vessel and the fittings used

for the vessel must be capable of safely withstanding the necessary extraction pressures, which range as high as 4900 psi (see Sec. 7.5). Check with the manufacturer of the particular extraction system for the maximum operating pressure and temperature of the system, as some vessels and fittings may not be capable of performing all of the extractions described in this method at the specified extraction pressures and temperatures.

4.1.2 Restrictor - This method was developed using continuously variable nozzle restrictors. Such restrictors have been found to be less likely than fixed nozzle restrictors to become plugged with ice derived from moisture in the sample. In addition, the recommended extraction fluids for some analytes to be analyzed via HPLC include mixtures of carbon dioxide, organic solvents, and water. Therefore, if other restrictors (e.g., tapered restrictors, static pinhole restrictors, frit restrictors, variable orifice restrictors, crimped metal tubing, or PEEK tubing) are employed, the analyst must demonstrate that the extraction and collection conditions described here (or modified by the laboratory) are appropriate for the analytes of interest in the matrix of interest. Such demonstrations are described in general in Method 8000, Sec. 8.

4.1.3 Collection device - This method is based on a solid trap used at both sub-ambient and above ambient temperatures for different sub-sets of the method. However, data are also presented on the use of a liquid trap (see Sec. 9.0).

4.1.3.1 When the analytes are collected in solvent, care must be taken in validation of the method, particularly for the first eight PAH compounds (Method 8310 elution order) which are often poorly recovered in liquid traps. The use of a glass wool plug in the inner tube of the collection vial improves recoveries. Flow must not be so high as to reduce the collection solvent to dryness. A 15-mL collection solvent volume is recommended.

4.1.3.2 When the analytes are trapped on a sorbent material, use ODS (Hypersil ODS was used to develop the method performance data for the solid sorbent trap), 30-40 micrometer particle diameter commonly used in solid phase extraction (SPE) cartridges. Other trapping materials have also been found to provide acceptable results, e.g. diol, however, if other material is used it should demonstrate equivalent trapping efficiency to the ODS.

4.2 Carbon dioxide cylinder balance (optional) - Balances from White Associates, Catalog No. 30, or Scott Specialty Gases Model 5588D, or equivalent, can be used to monitor the fluid usage. Such a device is useful because carbon dioxide tanks used for SFE are not equipped with regulators. This makes it difficult to determine when the tank needs to be replaced.

4.3 Filter paper disks to be placed at both ends of the sample. Disks may be cored from Whatman Qualitative filter paper, Catalog No. 1003-055, or equivalent; or from Baxter glass fiber filter paper, 0.5 µm, Catalog No. F232, 2-21, or equivalent.

5.0 REAGENTS

5.1 Carbon dioxide, CO_2 - Either supercritical fluid chromatography (SFC)- or SFE-grade CO_2 may be acceptable for use in SFE. However, SFC-grade CO_2 may contain more impurities then SFE-grade, and therefore may be unsuitable for trace analysis. Aluminum cylinders are generally preferred over steel cylinders. Depending on the specific instrumentation, the cylinders may need to be fitted with eductor tubes and the contents pressurized under 1500 psi of helium head pressure.

Consult the SFE system manufacturer's instructions regarding the specific cylinder configuration required.

5.2 Carbon dioxide (CO_2) for cryogenic cooling - Certain parts of some models of extractors (i.e., the high-pressure pump head and the analyte trap) must be cooled during use. The carbon dioxide used for this purpose must be dry, and should be supplied in tanks with full-length eductor tubes.

5.3 Modifiers (also called co-solvents) were added to the bulk CO_2 extraction fluid through the use of a separate (stand-alone) HPLC pump with the output joined in a TEE-piece to the flowing carbon dioxide stream after the carbon dioxide pump but before the extraction vessel. The modifier solvents are methanol, water, and methylene chloride (HPLC grade), forming extraction fluid mixtures of 95/1/4 (v/v/v) CO_2/methanol/water for HPLC analysis and 95/1/4 (v/v/v) CO_2/methanol/methylene chloride in the case where GC or GC/MS was used for the analytical measurement. There are concerns about the 4% water modifier leaving residual water in the collection trap that could have a detrimental effect on the gas chromatographic separation. Hence, the extraction fluid composition of 95/1/4 (v/v/v) CO_2/water/methanol should be altered to 95/1/4 (v/v/v) CO_2/methylene chloride/methanol - with some of the other parameters in the SFE method modified slightly as described in Section 7.0.

5.4 Reconstitution solvents - The reconstitution solvents dispensed by the SFE instruments using solid phase trapping may be the same material used for liquid trapping. This method was developed only with sub-ambient solid trapping. These same solvents were used to prepare the internal and external standard solutions. A 50/50 (v/v) mixture of acetonitrile/tetrahydrofuran (THF) was used when HPLC analysis was chosen: both were HPLC grade. A 75/25 (v/v) mixture of methylene chloride/isooctane was used when GC/MS was chosen for the analytical measurement. In addition, data from a different laboratory using a liquid trap are referenced in Sec. 9.3.

5.5 Surrogates - Recommended surrogates are bromobenzene (early eluter) and *p*-quaterphenyl (late eluter available from ChemService, West Chester, PA). Prepare a stock solution at a concentration of 10 g/L in a 50/50 (v/v) acetonitrile/THF mixture. Apply 150-µL aliquots to the soil samples within the extraction vessels at the exit end of the flow-through vessels. It has been observed that very small volumes (10 µL) of a concentrated surrogate mixture (100-1000 g/L) often gave poor recoveries while adding larger volumes of more dilute surrogate solution to the sample matrix achieved the expected recoveries.

5.6 Copper powder (electrolytic grade) - Added to samples which contain elemental sulfur. It is pretreated by sequentially rinsing 20 g with 150 mL of organic-free reagent water, 150 mL of acetone, 150 mL of hexane, and then drying in a rotary evaporator. The powder is then kept under argon until used. Copper powder must have a shiny bright appearance to be effective. If it has oxidized and turned dark it should not be used.

5.7 Sodium sulfate, anhydrous (12-60 mesh), Baker Analyzed or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Solid samples for this procedure should be collected and stored as any other solid samples containing semivolatile organics.

7.0 PROCEDURE

7.1 Sample handling - Decant and discard any water layer on a sediment sample. Mix the sample thoroughly, especially composited samples. Discard any foreign objects such as pieces of wood, glass, sticks, leaves and rocks.

7.2 Determination of sample % dry weight - In certain cases, sample results are desired based on dry-weight basis. When such data are desired, a separate portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination. Also, a moisture content in the sample between 10 - 50% for the GC/MS extraction method, provided the best extraction efficiency for the procedure as written. Therefore, determination of % moisture is necessary in this case.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.2.1 Immediately after weighing the sample for extraction, weigh an additional 5 - 10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

7.2.2 Calculate the % dry weight as follows:

$$\%\ \text{dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Safety considerations - Read Sec. 11.0, "Safety", before attempting to perform this procedure.

7.4 Sample grinding and homogenization.

NOTE: Sample grinding is a critical step in the SFE process. The soil/solid must be ground to a fine particle to ensure efficient extraction.

7.4.1 Mix at least 100 grams of sample with an equal volume of carbon dioxide solid "snow" prepared from the extraction grade carbon dioxide. Place this in a small food-type chopper, and grind for about one minute. Place the chopped sample on a clean surface and allow the carbon dioxide to sublime away. As soon as the sample appears free-flowing and without the solid carbon dioxide, weigh the sample and place in the extraction vessel. This procedure will ensure the homogeneity of the sample without loss of the volatile analytes and also retains the original moisture content of the sample.

7.4.2 Weigh 2.0 to 3.0 g of the homogenized sample into a pre-cleaned aluminum dish. (Up to 10 g of sample can be extracted using the conditions outlined in this procedure.) If sample moisture content exceeds 50%, add a plug (1 - 2 g) of anhydrous sodium sulfate (Sec. 5.7) next to the downstream frit in the extraction vessel. Do not add any drying agent of any kind directly to the sample. This method depends upon the controlled addition of water throughout the procedure. Any drying agents will interfere with the process.

7.4.3 For samples known to contain elemental sulfur, use copper powder (electrolytic grade) to remove the dissolved sulfur from the sample and carbon dioxide eluant. The copper powder (1 to 2 grams per sample) can be packed in a separate vessel between the extraction vessel and the nozzle (restrictor) or better, mixed with the sample in the extraction vessel itself.

Alternatively, a plug of copper powder may be placed in the extraction vessel beyond the sample before the exit-frits.

7.4.4 Transfer half of the weighed sample to the extraction vessel. Add 150 µL of surrogate solution to the sample in the vessel and then add the remainder of the sample material. To ensure efficient extraction, it is very important that the extraction vessel be completely full to avoid any dead volume. If any dead volume exists, fill the space with an inert, porous material, e.g., pre-cleaned Pyrex® glass wool, Celite®, etc.

7.5 Sample extraction - This section contains recommended extraction parameters for both HPLC and GC (including GC/MS) analyses.

NOTE: The CO_2/modifiers used for GC or GC/MS analysis extract more efficiently when the soil moisture content is between 10 to 50%. If the sample content is less than 10%, add 0.5 mL of water per gram of sample to the sample before placing it in the extraction vessel.

7.5.1 The following conditions for Step 1 (collection of the more volatile PAHs) are grouped according to function.

7.5.1.1 Extraction

Pressure:	1750 psi (120 bar)
Density:	0.30 g/mL
Extraction chamber temperature:	80°C
Extraction fluid composition:	CO_2
Static equilibration time:	10 minutes
Dynamic extraction time:	10 minutes
Extraction fluid flow rate:	2.0 mL/min

Resultant thimble-volumes-swept = 9.1 (this is equivalent to 20 mL of liquid carbon dioxide at a reference temperature of 4.0°C, density 0.96 g/mL or 19.2 g of carbon dioxide).

7.5.1.2 Collection (during extraction)

Trap packing:	ODS
Trap temperature:	-5°C
Nozzle temperature:	80°C (variable restrictor)

7.5.1.3 Reconstitution (of collected extracts)

Rinse solvent for HPLC:	50/50 (v/v) THF/acetonitrile
Rinse solvent for GC:	75/25 (v/v) CH_2Cl_2/isooctane
Collected fraction volume:	0.8 mL
Trap temperature:	60°C
Nozzle temperature:	45°C (variable restrictor)
Rinse solvent flow rate:	1.0 mL/min

The extract should be properly labeled with fraction designation and vial number.

7.5.2 The following conditions for Step 2 (collection of the lesser volatile PAHs) are grouped according to function.

7.5.2.1 Extraction

Pressure:	4900 psi (338 bar)
Density:	0.63 g/mL
Extraction chamber temperature:	120°C
Extraction fluid for HPLC:	95/1/4 (v/v/v) CO_2/methanol/water
Extraction fluid for GC:	95/1/4 (v/v/v) CO_2/methanol/CH_2Cl_2
Static equilibration time:	10 minutes
Dynamic extraction time:	30 minutes
Extraction fluid flow rate:	4.0 mL/min

Resultant thimble-volumes-swept = 25 (equivalent to 120 mL of liquid carbon dioxide at reference temperature of 4.0°C, density 1.06 g/mL or 127 g of carbon dioxide).

7.5.2.2 Collection (during Extraction)

Trap packing:	ODS
Trap temperature:	80°C
Nozzle temperature:	80°C (variable restrictor)

7.5.2.3 Reconstitution (of collected extracts) - none.

7.5.3 The following conditions for Step 3 (final sweep of modifiers) are grouped according to function.

7.5.3.1 Extraction

Pressure:	4900 psi (338 bar)
Density:	0.63 g/mL
Extraction chamber temperature:	120°C
Extraction fluid composition:	CO_2
Static equilibration time:	5 minutes
Dynamic extraction time:	10 minutes
$C0_2$ flow rate:	4.0 mL/min

Resultant thimble-volumes-swept = 8 (equivalent to 40 mL of liquid carbon dioxide at reference temperature of 4.0°C, density 1.06 g/mL or 42.4 g carbon dioxide).

7.5.3.2 Collection (during Extraction)

Trap packing:	ODS
Trap temperature:	80°C
Nozzle temperature:	80°C (variable restrictor)

NOTE: All three steps consume a total of 188.6 g of carbon dioxide.

7.5.3.3 Reconstitution (of collected extracts)

Rinse solvent for HPLC:	50/50 (v/v) THF/acetonitrile
Rinse solvent for GC:	75/25 (v/v) CH_2Cl_2/isooctane
Collected fraction volume:	0.8 mL
Trap temperature for HPLC:	80°C
Trap temperature for GC:	60°C
Nozzle temperature:	45°C (variable restrictor)
Rinse solvent flow rate:	1.0 mL/min

The extract should be properly labeled with fraction destination and vial number.

7.5.4 The combined extract volumes consist of 1.6 mL. The extract is ready for the analysis by Methods 8310 (HPLC), 8270 (GC/MS), or 8100 (GC/FID). Note that there are no performance data available on the analysis of SFE PAH extracts by Method 8100. Furthermore, the procedure is more susceptible to interferences in complex samples.

NOTE: If a fixed restrictor and liquid trapping are used, a restrictor temperature in the range of 100 to 150°C is recommended.

7.5.5 When GC or GC/MS analysis procedures are to be used and sulfur interference becomes apparent at time of analysis, Method 3660 may be used to remove the sulfur from the extract.

7.6 SFE System Maintenance

7.6.1 Depressurize the system following the manufacturer's instructions.

7.6.2 After extraction of an especially "tarry" sample, the end-frits of the extraction vessel may require replacement if not extensive cleanup to ensure adequate extraction fluid flow without excessive pressure drop due to the system plumbing. In addition, very fine particles may clog the exit frit requiring its replacement. By placing a layer of inert material such as Celite® or sea sand above the sample prior to the exit frit (and placing disks of filter paper on top of the inert material), this maintenance may be delayed for some period of operation.

7.6.3 Clean the extraction vessel after each extraction sample. The cleaning procedure depends upon the type of sample. After removing the bulk of the extracted sample matrix from the extraction vessel, the cell and end-frits should be scrubbed with an aqueous detergent, water and a stiff brush. Placing the parts in an ultrasonic bath with a warm detergent solution is very helpful. The parts should be rinsed with reagent water. The ultrasonic bath treatment should then be repeated with either methyl alcohol or acetone or both followed by air drying.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific Quality Control procedures and to Method 3500 for sample preparation quality control procedures.

8.2 Each time samples are extracted, and when there is a change in reagents, a reagent blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic

laboratory contamination. Any reagent blanks, matrix spike samples, or replicate samples should be subjected to exactly the same analytical procedures (Sec. 7.4) as those used on actual samples.

8.3 All instrument operation conditions and parameters should be recorded.

9.0 METHOD PERFORMANCE

9.1 Using Method 8310, an HPLC method with either UV/Vis or fluorescence detection, expected minimum detection limits are between 0.010 - 1.00 mg/kg depending upon the actual analyte and detector. The estimated quantitation limits (EQLs) would range from 0.10 - 10 mg/kg depending on analyte and detector. Using Method 8270, a GC/MS method, expected minimum detection limits are approximately 0.70 mg/kg. The estimated quantitation limits (EQLs) for GC/MS would be approximately 7 mg/kg. The MDLs and EQLs listed above are based on a 3-g sample.

9.2 Single laboratory precision and accuracy data based on this method (using a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of two reference materials (one a lake sediment from Environment Canada and the other a marine sediment from the National Science and Engineering Research Council of Canada, both naturally contaminated with PAHs). The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by GC/MS. The data were taken from Reference 2. Average recoveries from six replicate extractions ranged from 85 to 148% (overall average of 100%) based on the certified value (or a Soxhlet value if a certified value was unavailable for a specific analyte) for the lake sediment. Average recoveries from three replicate extractions ranged from 73 to 133% (overall average of 92%) based on the certified value for the marine sediment. The data are found in a table in Method 8270.

9.3 Single laboratory precision and accuracy data based on the use of a fixed restrictor and liquid trapping were obtained for twelve of the method analytes by the extraction of a certified reference material obtained from Fisher Scientific (a soil naturally contaminated with PAHs). The SFE instrument used for these extractions was a Dionex Model 703-M. Analysis was by GC/MS. Average recoveries from four replicate extractions ranged from 60 to 122% (overall average of 89%) based on the certified value. Following are the instrument conditions that were utilized to extract a 3.4 g sample: Pressure - 300 atm; Time - 60 min.; Extraction fluid - CO_2; Modifier - 10% 1:1 (v/v) methanol/methylene chloride; Oven temperature - 80°C; Restrictor temperature - 120°C; and, Trapping fluid - chloroform (methylene chloride has also been used). The data are found in a table in Method 8270.

9.4 Single laboratory precision and accuracy data based on this method (using a variable restrictor and solid trapping material) were obtained for the method analytes by the extraction of a well-characterized reference material naturally contaminated with PAHs. The SFE instrument used for these extractions was a Hewlett-Packard Model 7680. Analysis was by HPLC. Average recoveries from three replicate extractions ranged from 85.7 to 153% (overall average of 107%) based on the Soxhlet value. The data may be incorporated in a future revision of Method 8310.

10.0 REFERENCES

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5. S. Bowadt and B. Johansson, "Analysis of PCBs in Sulfur-Containing Sediments by Off-Line SFE", Analytical Chemistry, 66, No. 5, 667 (1994).

11.0 SAFETY

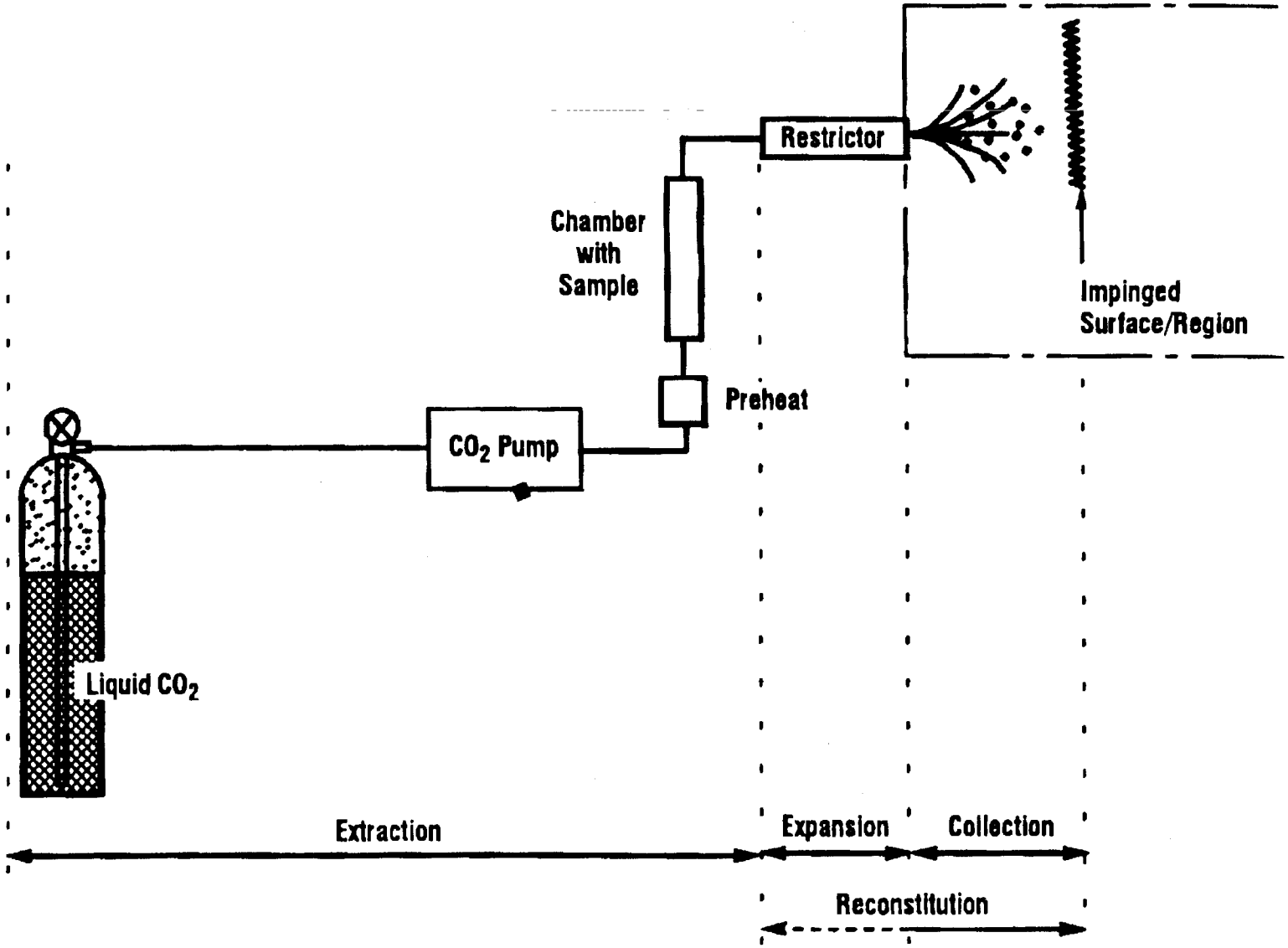
11.1 When liquid carbon dioxide comes in contact with skin, it can cause "burns" because of its low temperature (-78°C). Burns are especially severe when CO_2 is modified with organic liquids.

11.2 The extraction fluid, which may contain a modifier, usually exhausts through an exhaust gas and liquid waste port on the rear of the panel of the extractor. This port must be connected to a chemical fume hood to prevent contamination of the laboratory atmosphere.

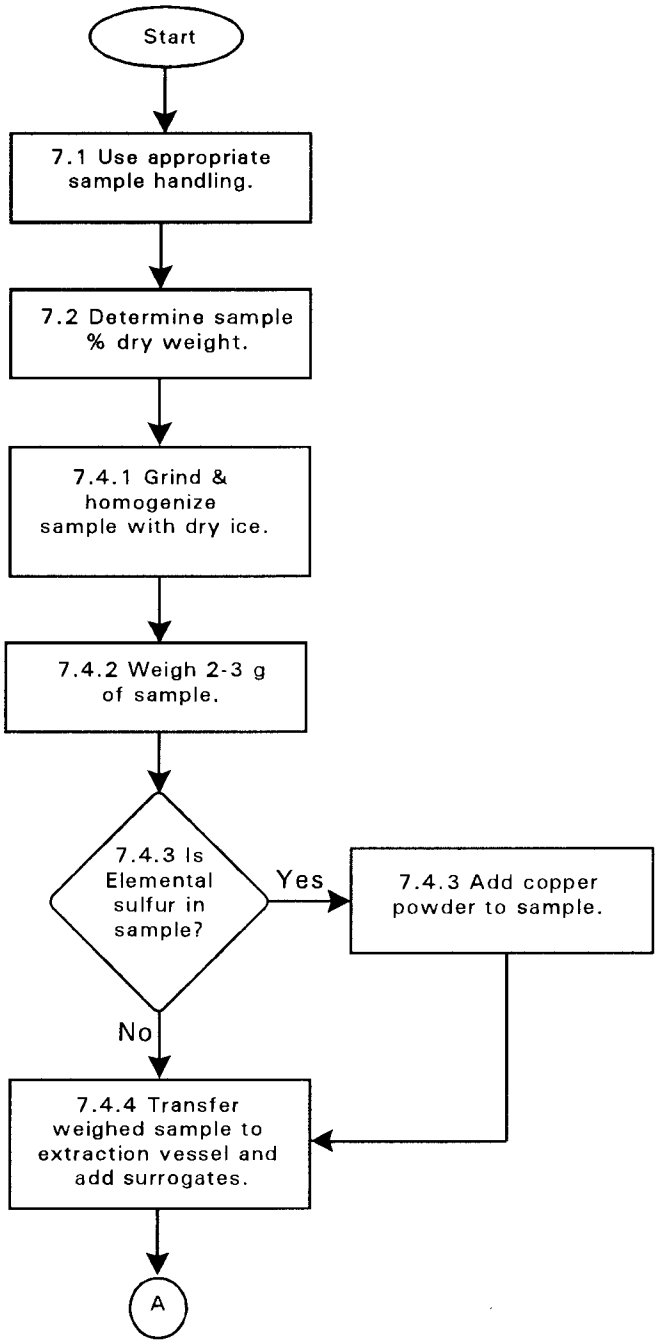
11.3 Combining modifiers with supercritical fluids requires an understanding and evaluation of the potential chemical interaction between the modifier and the supercritical fluid, and between the supercritical fluid or modifier and the analyte(s) or matrix.

11.4 When carbon dioxide is used for cryogenic cooling, typical coolant consumption is 5 L/min, which results in a carbon dioxide level of 900 ppm for a room of 4.5 m x 3.0 m x 2.5 m, assuming 10 air exchanges per hour.

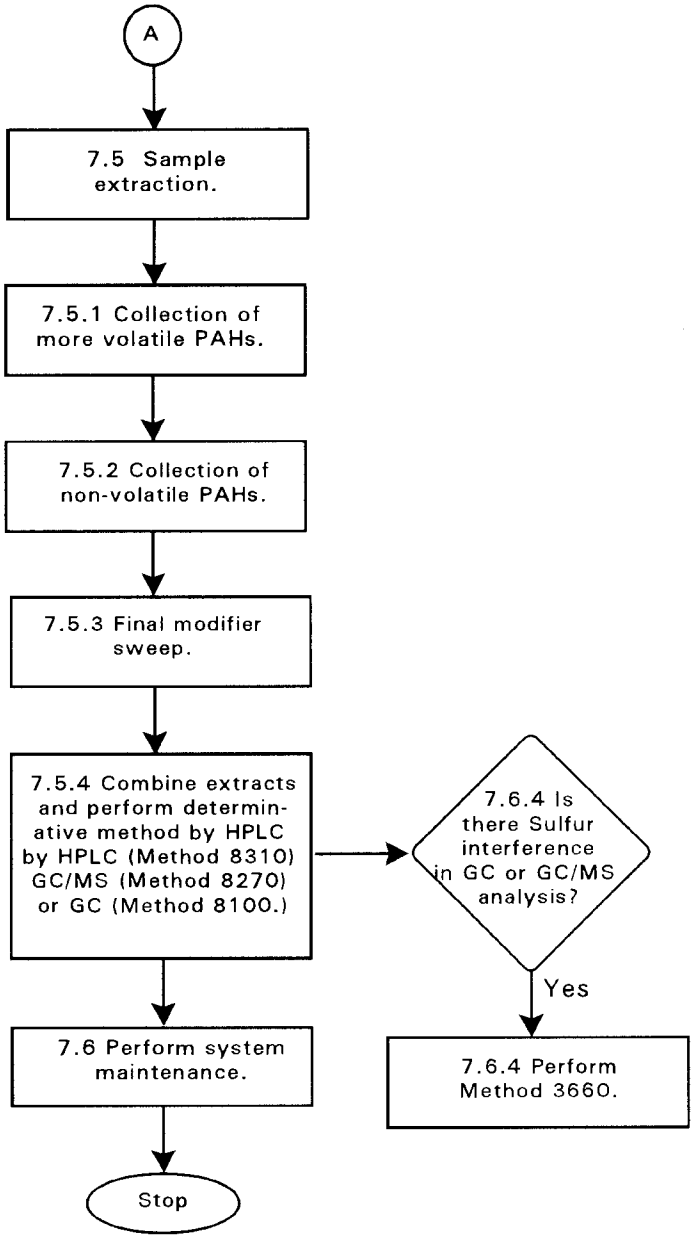
FIGURE 1
SCHEMATIC OF A TYPICAL SUPERCRITICAL FLUID EXTRACTION SYSTEM



SUPERCRITICAL FLUID EXTRACTION OF POLYNUCLEAR AROMATIC HYDROCARBONS



SUPERCRITICAL FLUID EXTRACTION OF POLYNUCLEAR AROMATIC HYDROCARBONS



USEPA METHOD 3562

SUPERCRITICAL FLUID EXTRACTION OF POLYCHLORINATED BIPHENYLS (PCBs) AND ORGANOCHLORINE PESTICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 3562 describes the extraction with supercritical fluids of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) from soils, sediments, fly ash, solid-phase extraction media, and other solid materials which are amenable to extraction with conventional solvents. The method is suitable for use with any supercritical fluid extraction (SFE) system that allows extraction conditions (e.g., pressure, temperature, flow rate) to be adjusted to achieve separation of the PCBs and OCPs from the matrices of concern. The following compounds have been extracted by this method during validation studies. Similar compounds not listed should also be amenable to this extraction.

Compound	CAS Registry No.	IUPAC No.
2,4,4'-Trichlorobiphenyl	7012-37-5	28
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	52
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	101
2,3,3',4,4'-Pentachlorobiphenyl	32598-14-4	105
2,3',4,4',5-Pentachlorobiphenyl	31508-00-6	118
2,2',3,3',4,4'-Hexachlorobiphenyl	38380-07-3	128
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	138
2,2',3,4',5',6-Hexachlorobiphenyl	38380-04-0	149
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	153
2,3,3',4,4',5'-Hexachlorobiphenyl	38380-08-4	156
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	170
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	180
Aldrin	309-00-2	
β-Hexachlorocyclohexane (β-BHC)	319-85-7	
δ-Hexachlorocyclohexane (δ-BHC)	319-86-8	
γ-Hexachlorocyclohexane (γ-BHC, or Lindane)	58-89-9	
α-Chlordane	5103-71-9	
4,4'-DDD	72-54-8	
4,4'-DDE	72-55-9	
4,4'-DDT	50-29-3	
Dieldrin	60-57-1	
Endosulfan II	33213-65-9	
Endrin	72-20-8	
Endrin aldehyde	7421-93-4	
Heptachlor	76-44-8	
Heptachlor epoxide	1024-57-3	

1.2 Method 3562 is not suitable for the extraction of PCBs or organochlorine pesticides from liquid samples without some treatment of the liquid before introduction into the SFE to "stabilize" the liquid. Otherwise, the sample may be extruded through the end pieces of the extraction vessel without the benefit of SFE. The use of solid-phase extraction (SPE) media is one way to stabilize a liquid sample and it allows an easy coupling of two selective sample preparation techniques. The use of large diameter (ca. 90 mm) SPE disks coupled with SFE allows large volumes of aqueous samples to be prepared without the need for organic solvent elution. Furthermore, SFE may allow an in-line cleanup to be performed, thus eliminating the need for separate column cleanup and subsequent solvent concentration steps.

1.3 The extraction conditions listed in this procedure (Sec. 11.6) employed a variable restrictor and solid trapping media. Other extraction conditions and equipment are acceptable once appropriate method performance is demonstrated. The method applicability demonstration should be based on the extraction of a certified reference sample or an environmentally-contaminated sample, not on spiked soil/solids, whenever possible. It should be noted that there are currently no "certified" samples for organochlorine pesticides. An authentic, weathered, environmental sample which has been extracted by a traditional sample preparation technique should be used as the reference for these compounds.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 In order to assure a homogeneous sample and minimum subsampling errors, at least 100 g of sample are homogenized with an equal volume of solid CO_2 “snow”. A 1 - 5 g aliquot of this mixture is packed into a stainless steel SFE extraction vessel. Copper powder may be added to the cell to remove sulfur from the sample extract. Surrogates and/or internal standards are added to the portion of the sample in the cell and the cell is placed in the SFE extraction device.

2.2 The sample is extracted using supercritical carbon dioxide with no modifiers. Samples to be analyzed for PCBs are subjected to a 10-minute static extraction, followed by a 40-minute dynamic extraction. Samples for organochlorine pesticides are subjected to a 20-minute static extraction, followed by a 30-minute dynamic extraction.

2.3 The sample extract is trapped on a solid-phase sorbent (Florisil for PCBs and octadecyl silane for pesticides). The trapping material is then rinsed with solvent to collect the analytes of interest and reactivate the trapping material for reuse.

2.4 The sample extracts may be subjected to additional cleanup steps (see Method 3600) and then analyzed by the appropriate determinative methods.

3.0 DEFINITIONS

Dynamic extraction - An application of SFE in which the supercritical extraction fluid flows through the sample and out of the extraction cell to a collection device during the extraction. Dynamic extraction is contrasted with static extraction (see below).

Modifier - A liquid or gaseous component added to the supercritical fluid to change its extraction capabilities, often through changes in the solvation power of the extraction fluid. Modifiers may be polar or nonpolar.

Supercritical fluid - A gas maintained above its critical temperature through the application of pressure.

Supercritical fluid extraction (SFE) - The use of a gas maintained above its critical temperature as an extraction fluid.

Static extraction - An application of SFE in which the supercritical extraction fluid is held in the extraction vessel during the entire procedure, and is then released to a collection device. Static extraction is contrasted with dynamic extraction (see above).

4.0 INTERFERENCES

4.1 The analyst must demonstrate through the analysis of method blanks that the supercritical fluid extraction system is free from interferants. To do this, perform a simulated extraction using an empty extraction vessel and a known amount of CO_2 under the same conditions as those used for sample extraction, and determine the background contamination by analyzing the extract by the determinative method that will be used for sample analysis.

4.2 The extraction vessel(s), the end-frits, the nozzle restrictor(s), and the multi-port valve(s) may retain solutes whenever high-concentration samples are extracted. Therefore, it is good practice to clean the extraction system after such extractions. Suspect parts of the system should be replaced when reagent blanks indicate carryover. At least one reagent blank should be prepared and analyzed daily when the instrument is in use. Furthermore, reagent blanks should be prepared and analyzed after each extraction of a high-concentration sample (high part per million range). If reagent blanks continue to indicate contamination, even after replacement of the extraction vessel (and the restrictor, if a fixed restrictor system is used), then the multi-port valve must be cleaned. The operator must be ever vigilant against impurities arising from liquid solvents and CO_2 itself. Avoid any apparatus, valves, solenoids, and other hardware that contain lubricants or chlorofluorohydrocarbon materials that can serve as background contaminant sources.

4.3 No modifier was employed in the development of this method for either PCBs or organochlorine pesticides. Use of a modifier may cause many other problems in these samples. If the method is modified by the user to include an on-line modifier, or pre-mixed tanks of CO_2 and modifier, considerable effort must be made to validate this change.

4.4 Refer to Method 3500, Section 3.0, for general extraction interference guidance.

5.0 SAFETY

5.1 SFE involves the use of high pressure gases. Typical SFE systems have maximum operating pressures of approximately 400 atm (6000 psi). Great care must be taken to ensure that *all* components of the system are capable of withstanding such pressures.

5.2 SFE also involves heating portions of the system above ambient temperature, resulting in further increases in pressure. The combined effects of the starting pressure and temperature increase must be taken into account when evaluating the capabilities of system components.

5.3 SFE devices typically employ gases at high pressure directly from a tank, with no pressure regulator. In addition to making it difficult to monitor the level of gas in the tank, the lack of a regulator means that system leaks may involve gases at 2000 psi or more.

5.4 When liquid CO_2 comes in contact with skin, it can cause "burns" because of its low temperature (-70°C). Burns are especially severe when $C0_2$ is modified with organic liquids.

5.5 The extraction fluid usually exhausts through an exhaust gas and liquid waste port on the rear of the panel of the extractor. This port must be connected to a chemical fume hood to prevent contamination of the laboratory atmosphere.

5.6 Combining modifiers with supercritical fluids requires an understanding and evaluation of the potential chemical interaction between the modifier and the supercritical fluid, and between the supercritical fluid and/or modifier and the analyte(s) or matrix.

5.7 When CO_2 is used for cryogenic cooling, typical coolant consumption is 5 L/min, which results in a CO_2 level of 900 ppm for a room of 4.5 m x 3.0 m x 2.5 m, assuming 10 air exchanges per hour.

6.0 EQUIPMENT AND SUPPLIES

6.1 Supercritical fluid extractor and associated hardware - Any supercritical fluid extraction system that can achieve the extraction conditions and performance specifications detailed in this procedure may be used.

WARNING: *A safety feature to prevent over-pressurization is required on the extractor. This feature should be designed to protect the laboratory personnel and the instrument from possible injuries or damage resulting from equipment failure under high pressure.*

6.1.1 Extraction vessel - Stainless-steel vessel with end fittings with 2 μm frits. Use the extraction vessel supplied by the manufacturer of the SFE system being used. Fittings used for the extraction vessel must be capable of withstanding the required extraction pressures. The maximum operating pressure for most extractors is 400 atm. Pressures above 400 atm, especially at elevated temperatures, are likely to exceed the ratings of standard chromatography tubing and fittings. Check with the manufacturer of the particular extraction system and especially the tubing manufacturer for the maximum operating pressure and temperature for that system. Make sure that the extraction vessels are rated for such pressures and temperatures.

6.1.2 Restrictor - This method was developed with continuously variable nozzle restrictors that do not require that the operator take steps to remove water from the sample. If a fixed restrictor is used, additional validation must be done to verify that moisture from the sample does not adversely affect the chromatography of the determinative step.

6.1.3 Collection device - This method is based on a solid trap used at sub-ambient and above ambient temperatures for the different classes of analytes (PCBs vs. OCPs). However, a liquid (solvent) trap may also be used.

6.1.3.1 Use Florisil, 30-40 μm particle diameter (commonly used in SPE cartridges), as a solid trap for the PCBs.

6.1.3.2 For organochlorine pesticides, octadecyl silane (ODS) may be used as a solid trap, although the use of Florisil is also possible.

6.1.3.3 Analytes may be collected in a small volume of solvent in a suitable vial, however, great care must be taken to recover the most volatile compounds. The use of a glass wool plug in the inner tube of the collection vial

improves recoveries. Gas flow must not be so high as to evaporate the collection solvent to dryness. A 15-mL collection solvent volume is recommended.

6.2 CO_2 cylinder balance (optional) - Balances from Scott Specialty Gases, Model 5588D, or equivalent, may be used to monitor the fluid usage. Such a device is useful because CO_2 tanks used for SFE are not equipped with regulators, and it is difficult to determine when the tank needs to be replaced.

6.3 Glass microfiber filter paper disks - Cored out of Whitman QF/F filter paper (Whatman No. 1825021), or equivalent. A disk is placed at both ends of the sample. This ultra-fine filter paper has good retentive properties for particulate matter down to 0.7 μm and is easy to core. The normal background is insignificant, but blanks must be run on each batch.

7.0 REAGENTS AND STANDARDS

7.1 CO_2 - SFE-grade CO_2 is absolutely necessary for use in SFE. Aluminum cylinders are preferred to steel cylinders. The cylinders must be fitted with eductor tubes.

7.2 CO_2 for cryogenic cooling - Certain parts of some models of extractors (i.e., the high-pressure pump head and the analyte trap) must be cooled during use. The CO_2 used for this purpose must be supplied in tanks with a full-length eductor tube, but need not be SFE-grade. A low-cost industrial grade is acceptable.

7.3 Reconstitution solvents - The reconstitution solvents dispensed by the SFE instruments that use solid-phase trapping may be the same solvent that is used for liquid trapping. This method was developed with only sub-ambient solid trapping. Liquid trapping will work for this method as well, however the trapping volume is typically ten times larger than that with a solid trap. Further, the use of liquid trapping will likely require the use of manual Florisil or silica cleanup. These manual cleanup steps will also require the concentration of the solvent after the cleanup, a step that can be avoided through use of solid-phase trapping.

7.4 Internal Standards - Refer to the appropriate determinative method for information of the choice of internal standards, where applicable. However, note that for PCBs, certain ethers work well as internal standards, but do not survive the SFE extraction particularly well.

7.4.1 Internal standards for PCBs - Internal standards that have been evaluated using this method include PCB 35, PCB 36, PCB 169, 2,4-dichlorobenzyl hexyl ether, 2,4-dichlorobenzyl heptyl ether, 1,2,3,4-tetrachloronaphthalene, hexabromobenzene, and octachloronaphthalene.

7.4.2 Internal standard for organochlorine pesticides - Pentachloronitrobenzene

7.5 Surrogate standards - Refer to the appropriate determinative method for information of the choice of surrogates. Surrogates that have been evaluated using this method include hexabromobenzene, PCB 35, PCB 36, PCB 169, 1,2,3,4-tetrachloronaphthalene, and octachloronaphthalene. Prepare a stock solution of 10 mg/mL. Apply 150-μL aliquots to the soil samples within the extraction vessels at the exit end of the flow-through vessels. It has been observed that a very small volume (10 μL) of a concentrated surrogate mixture often gives poor recoveries, while adding a larger volume of more dilute surrogate standard to the sample matrix achieved the expected recoveries.

7.6 Copper powder - Electrolytic grade. Added to samples that contain elemental sulfur. The powder is pretreated by rinsing 20 g with 150 mL organic-free reagent water, 150 mL acetone, 150 mL of hexane, and drying in a rotary evaporator. The powder is kept under

argon or helium until used. Copper powder must have a shiny bright appearance to be effective. If it has oxidized and turned dark, it should not be used.

7.7 Sodium Sulfate - Anhydrous (12-60 mesh), Baker Analyzed grade, or equivalent.

7.8 Celite 545 - 60/80 mesh, J. T. Baker, or equivalent. Prepare a reagent blank to assure that no background contaminants are present.

7.9 Solvents - Used for eluting the analytes of interest from the solid trapping material and rinsing the trapping material prior to reuse. All solvents should be pesticide-grade or equivalent.

7.9.1 n-Heptane, C_7H_{16}

7.9.2 Methylene chloride, CH_2Cl_2

7.9.3 Acetone, CH_3COCH_3

7.10 Florisil - Pesticide residue grade.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

8.2 Solid samples to be extracted by this procedure should be collected and stored as any other solid samples containing semivolatile organics.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One and Method 8000 for specific Quality Control procedures and to Method 3500 for sample preparation quality control procedures.

9.2 Each time samples are extracted, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. Any method blanks, matrix spike samples, or replicate samples should be subjected to the same analytical procedures (Sec. 11) as those used on actual samples.

9.3 All instrument-operating conditions should be recorded.

10.0 CALIBRATION AND STANDARDIZATION

There are no calibration or standardization steps associated with this sample extraction procedure other than establishing the extraction conditions in Sec. 11.6.

11.0 PROCEDURE

11.1 Sample handling - Decant and discard any water layer on a sediment sample. Discard any foreign objects such as pieces of wood, glass, leaves and rocks.

11.2 Determination of sample % dry weight - In certain cases, sample results are desired based on dry-weight basis. When such data are desired, a separate portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: *The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.*

11.2.1 Immediately after weighing the sample aliquot to be extracted, weigh an additional 5 - 10 g aliquot of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

11.2.2 Calculate the % dry weight as follows:

11.3 Sample grinding and homogenization

NOTE: *Sample grinding is a critical step in the SFE process. The soil/solid must be a fine particle to ensure efficient extraction.*

11.3.1 Mix at least 100 grams of sample with an equal volume of CO_2 solid "snow" prepared from the extraction grade CO_2. Place this mixture in a small food-type chopper, and grind for two minutes. Place the chopped sample on a clean surface and allow the CO_2 to sublime away. As soon as the sample appears free-flowing and solid CO_2 is no longer visible, weigh the sample and place it in the extraction vessel. This procedure will ensure the homogeneity of the sample without loss of the volatile analytes and also retains the original moisture content of the sample.

11.3.2 Weigh 1.0 to 5.0 g of the homogenized sample from Sec. 11.3.1 into a pre-cleaned aluminum dish. For samples in the mg/kg (ppm) concentration range, use a 0.1-gram sample after carefully homogenizing (Sec. 11.3.1) the bulk sample, to avoid sub-sampling errors.

11.4 For samples known to contain elemental sulfur, use copper powder (Sec. 7.6) to remove the dissolved sulfur from the sample and CO_2 eluant. The copper powder (1 to 2 grams per sample) can be mixed with the sample in the extraction vessel itself, or packed in a separate vessel between the extraction vessel and the nozzle (restrictor). The copper addition to samples is a useful precaution, whether or not one suspects the presence of elemental sulfur. In tests, no adverse effect from the addition of copper was observed and it appears that finely divided copper may enhance the dispersion of CO_2. If copper powder is added to the samples, it must also be added to the method blank.

11.5 Packing the extraction cell

The procedure used for a 7.0-mL SFE extraction vessel with sample and copper powder is as follows:

11.5.1 Place a small disk of fiber glass filter paper at the bottom of the extraction vessel to protect the end frits from particulate matter (this makes the cleanup very easy between samples and lessens any chance of plugging of the frits).

11.5.2 Place approximately two grams of anhydrous sodium sulfate on top of this disk in the extraction vessel. Weigh 1.0 gram of solid waste sample into a weighing dish. Add two grams of electrolytic grade copper powder to the same weighing dish, followed by 7 grams of anhydrous sodium sulfate. Mix the weighed material. Transfer the entire homogeneous mixture to the extraction vessel on top of the existing small layer of sodium sulfate. Finally, place a top layer (2 grams) of sodium sulfate on top of the mixture. The densities of the respective materials are such that this still leaves a small volume at the top of a 7-mL vessel. These ratios may be adjusted for different sample sizes and vessel sizes, but should be kept consistent among samples and blanks.

11.5.3 If a surrogate is being added, transfer half the weighed sample to the extraction vessel. Add 150 μL of surrogate standard to the sample in the vessel and then add the remainder of the sample material.

11.5.4 To ensure efficient extraction, fill the extraction vessel completely, avoiding any dead volume. If any dead volume remains, fill the space with an inert, porous material, e.g., pre-cleaned Pyrex glass wool, Celite, etc.

11.6 Sample extraction conditions

11.6.1 Recommended conditions for PCBs

11.6.1.1 Extraction conditions

Pressure:	4417 psi (305 bar)
Extraction chamber temperature:	80°C
Density:	0.75 g/mL
Extraction fluid composition:	CO_2
Static equilibration time:	10 minutes
Dynamic extraction time:	40 minutes
Extraction fluid flow rate:	2.5 mL/minute

The resultant thimble volume swept is 17.6 times the volume of the cell at 1 bar (this is equivalent to 100 mL of liquid CO_2 at a reference temperature of 4.0°C and a density 0.92 g/mL, or 92 g of CO_2).

11.6.1.2 Collection conditions (during extraction)

Trap packing:	Florisil
Trap temperature:	15-20°C
Nozzle temperature:	45-55°C (variable restrictor)

11.6.1.3 Reconstitution conditions for collected extracts

The reconstitution process consists of four rinse steps. The first rinse is used to elute the analytes of interest from the trapping material. All four rinse steps are performed with a recommended trap temperature of 38°C, a nozzle temperature of 30°C, and a flow rate of 1.0 mL/min.

Rinse Substep 1:

Rinse solvent	n-Heptane
Collected rinse volume:	1.6 mL

Rinse Substep 2:

Rinse solvent	n-Heptane
Collected rinse volume:	1.6 mL

This second rinse step is an "insurance rinse". The vial is usually not analyzed unless there is a need or desire to assure that the entire sample rinsed in substep 1.

Rinse Substep 3:

Rinse solvent	Methylene chloride:Acetone (1:1)
Collected rinse volume:	4.0 mL (to waste)

This third rinse step provides a means of rinsing the solid Florisil trap to remove interfering compounds such as lipids, hydrocarbons, and PAHs. The rinse solvent is then discarded.

Rinse Substep 4:

Rinse solvent	n-Heptane
Collected rinse volume:	3.0 mL (to waste)

This fourth rinse step provides a means of regenerating the solid Florisil trap to prepare it (reactivate) for reuse.

11.6.2 Recommended conditions for organochlorine pesticides

11.6.2.1 Extraction conditions

Pressure:	4330 psi (299 bar)
Extraction chamber temperature:	50°C
Density:	0.87 g/mL
Extraction fluid composition:	CO_2

Static equilibration time:	20 minutes
Dynamic extraction time:	30 minutes
Extraction fluid flow rate:	1.0 mL/minute

The resultant thimble volume swept is 4.6 times the volume of the cell at 1 bar (this is equivalent to 30 mL of liquid CO_2 at a reference temperature of 4.0°C and a density 0.92 g/mL, or 28 g of CO_2).

11.6.2.2 Collection conditions (during extraction)

Trap packing:	ODS
Trap temperature:	20°C
Nozzle temperature:	50°C (variable restrictor)

11.6.2.3 Reconstitution conditions for collected extracts

The extraction of organochlorine pesticides requires only a single rinse step.

Rinse solvent:	n-Hexane
Collected fraction volume:	1.3 mL
Trap temperature:	50°C
Nozzle temperature:	30°C (variable restrictor)
Rinse solvent flow rate:	2 mL/minute

NOTE: If a fixed restrictor and liquid trapping are used, a restrictor temperature between 100 and 150°C is recommended.

11.7 Label the extract with the fraction designation and vial number.

11.8 If the copper powder was not added to the sample prior to loading the cell, additional sulfur cleanup of the extracts may be required prior to analysis.

11.9 SFE System Maintenance

11.9.1 Depressurize the system following the manufacturer's instructions.

11.9.2 After extraction of an especially "tarry" sample, the end-frits of the extraction vessel may require extensive cleanup or replacement to ensure adequate flow of extraction fluid without an excessive pressure drop. In addition, very fine particles may clog the exit frit, necessitating its replacement. By placing a layer of inert material such as Celite or sand between the sample and the exit frit (and placing disks of filter paper or glass fiber filter on top of the inert material), this maintenance may be delayed.

11.9.3 Clean the extraction vessel after each sample extraction. The cleaning procedure depends upon the type of sample. After removing the bulk of the extracted sample from the extraction vessel, the cell and end-frits should be scrubbed with a solution of detergent and water using a stiff brush. Placing the parts in an ultrasonic bath with a warm detergent solution may help. Rinse the parts with organic-free reagent water. Repeat the ultrasonic bath treatment with either methyl alcohol, or acetone, or both, followed by air drying.

12.0 DATA ANALYSIS AND CALCULATIONS

There are no calculations explicitly associated with this extraction procedure. See the appropriate determinative method for calculation of final sample results.

13.0 METHOD PERFORMANCE

13.1 Tables in Method 8081 contain single laboratory performance data for the organochlorine pesticides using supercritical fluid extraction Method 3562 on an HP 7680. Samples were analyzed using GC/ELCD. The method was performed using a variable restrictor and solid trapping material. Three different soil samples were spiked at 5 and 250 ug/kg. Soil 1

(Delphi) is described as loamy sand, with 2.4% clay, 94% sand, 0.9% organic matter, 3.4% silt, and 0.1% moisture. Soil 2 (McCarthy) is described as sandy-loam, with 11% clay, 56% sand, 22% organic matter, 33% silt, and 8.7% moisture. Soil 3 (Auburn) is described as clay loam, with 32% clay, 21% sand, 5.4% organic matter, 46% silt, and 2.2% moisture. Seven replicate extractions were made of each soil at the 2 concentrations.

13.2 Tables in Method 8082 contain laboratory performance data for several PCB congeners using supercritical fluid extraction Method 3562 on an HP 7680. Seven replicate extractions on each sample were performed. The method was performed using a variable restrictor and solid trapping material (Florisil). Sample analysis was performed by GC/ECD. The following soil samples were used for this study:

13.2.1 Two field-contaminated certified reference materials were extracted by a single laboratory. One of the materials was a lake sediment from Environment Canada (EC-5). The other material was soil from a dump site and was provided by the National Science and Engineering Research Council of Canada (EC-1). The average recoveries for EC-5 are based on the certified value for that sample. The average recoveries for EC-1 are based on the certified value of the samples or a Soxhlet value, if a certified value was unavailable for a specific analyte.

13.2.2 Four certified reference materials were extracted by two independent laboratories. The materials were: a marine sediment from NIST (SRM 1941), a fish tissue from NIST (SRM 2974), a sewage sludge from BCR European Union(CRM 392), and a soil sample from BCR European Union (CRM 481). The average recoveries are based on the certified value of the samples or a Soxhlet value, if a certified value was unavailable for a specific analyte.

13.2.3 A weathered sediment sample from Michigan (Saginaw Bay) was extracted by a single laboratory. Soxhlet extractions were carried out on this sample and the SFE recovery is relative to that for each congener. The average recoveries are based on the certified value of the samples. Additional data is shown in the tables for some congeners that were not certified.

14.0 POLLUTION PREVENTION

Extraction of organic compounds using supercritical fluid extraction conforms with EPA's pollution prevention goals. The volumes of solvent employed, if any, are significantly smaller than with other extraction procedures. Minimal waste is generated.

15.0 WASTE MANAGEMENT

Laboratory waste management procedures must be consistent with federal, state, and local regulations.

16.0 REFERENCES

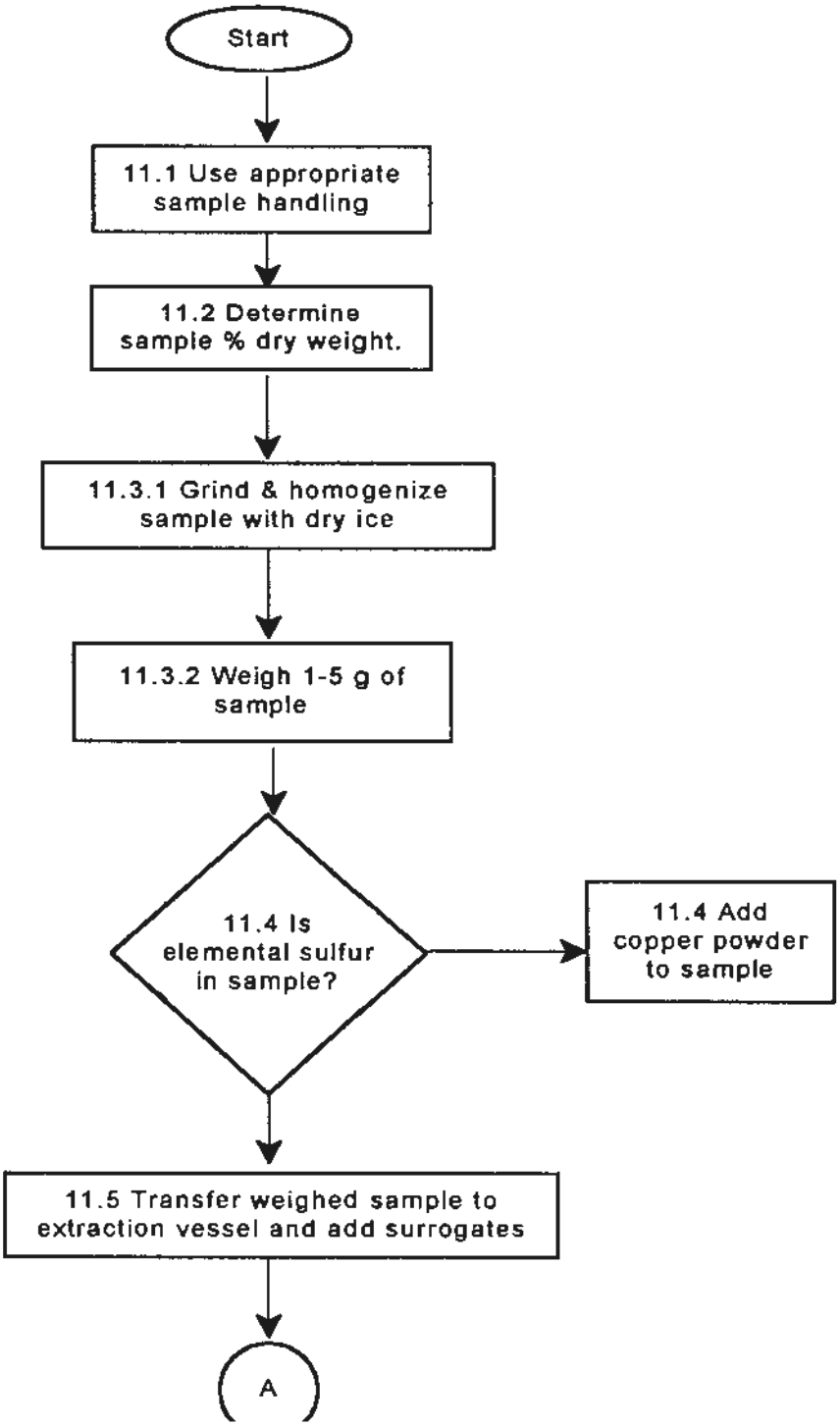
Gere, D, “Final Deliverables for PCB/OCP SFE Draft Method,” letter to B. Lesnik, April 15, 1995.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

A flow diagram for the method procedure follows.

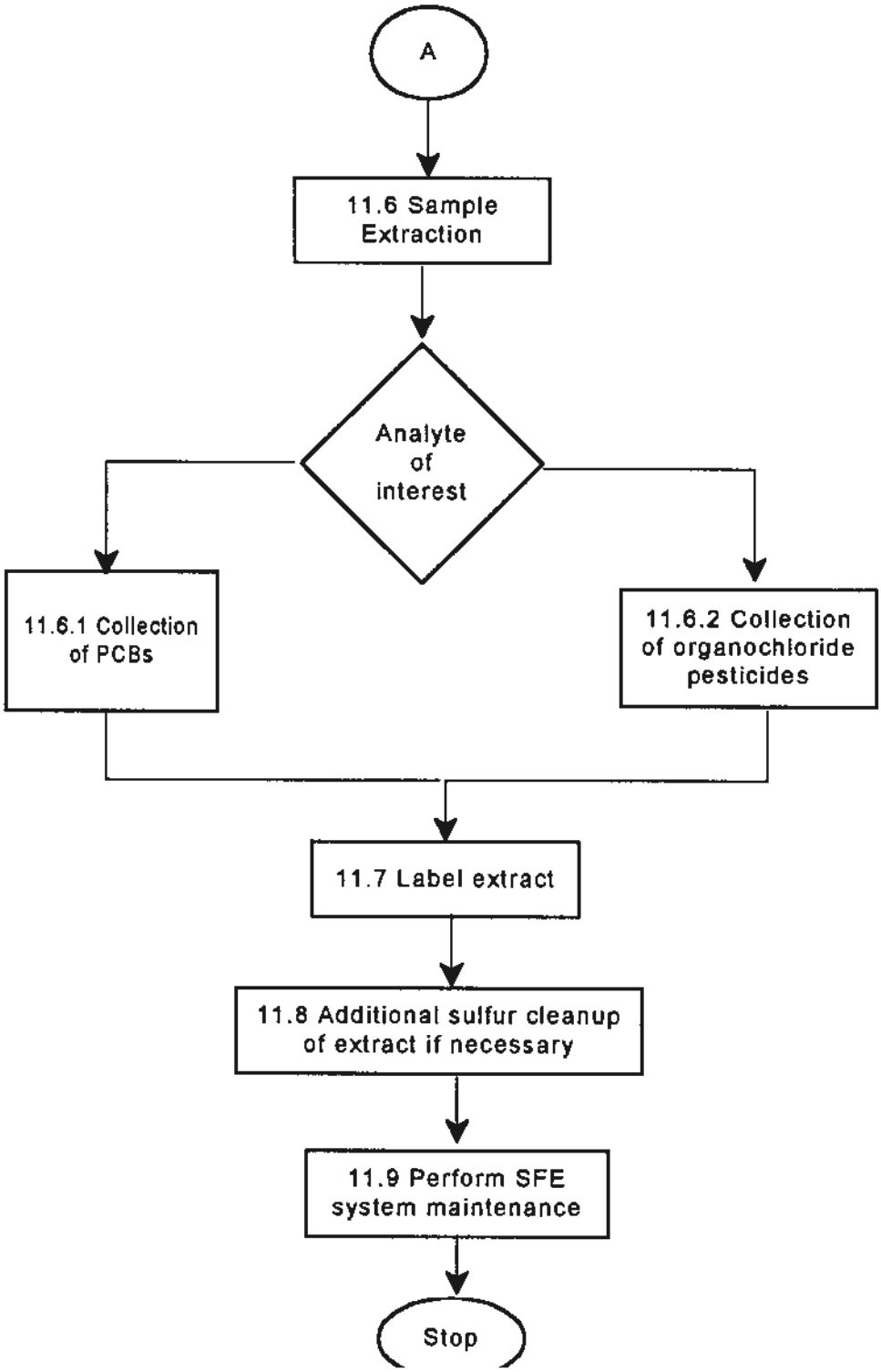
METHOD 3562

SUPERCRITICAL FLUID EXTRACTION OF POLYCHLORINATED BIPHENYLS (PCBs) AND ORGANOCHLORINE PESTICIDES.


Start
11.1 Use appropriate sample handling
11.2 Determine sample % dry weight.
11.3.1 Grind & homogenize sample with dry ice
11.3.2 Weigh 1-5 g of sample
11.4 Is elemental sulfur in sample?
11.4 Add copper powder to sample
11.5 Transfer weighed sample to extraction vessel and add surrogates
A

METHOD 3562

(Continued)


A
11.6 Sample Extraction
Analyte of interest
11.6.1 Collection of PCBs
11.6.2 Collection of organochloride pesticides
11.7 Label extract
11.8 Additional sulfur cleanup of extract if necessary
11.9 Perform SFE system maintenance
Stop

METHOD 3580A

WASTE DILUTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a solvent dilution of a non-aqueous waste sample prior to cleanup and/or analysis. It is designed for wastes that may contain organic chemicals at a concentration greater than 20,000 mg/kg and that are soluble in the dilution solvent.

1.2 It is recommended that an aliquot of the diluted sample be cleaned up. See this chapter, Organic Analytes, Section 4.2.2 (Cleanup).

2.0 SUMMARY OF METHOD

2.1 One gram of sample is weighed into a capped tube, and the sample is diluted to 10.0 mL with an appropriate solvent.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Glass scintillation vials: At least 20 mL, with Teflon or aluminum foil lined screw-cap, or equivalent.

4.2 Spatula: Stainless steel or Teflon.

4.3 Balance: Capable of weighing 100 g to the nearest 0.01 g.

4.4 Vials and caps: 2 mL for GC autosampler.

4.5 Disposable pipets: Pasteur.

4.6 Test tube rack.

4.7 Pyrex glass wool.

4.8 Volumetric flasks, Class A: 10 mL (optional).

5.0 REAGENTS

5.1 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride,

a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.2 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.3 Hexane, C_6H_{14} - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Samples consisting of multiphases must be prepared by the phase separation method (Chapter Two) before extraction.

7.2 The sample dilution may be performed in a 10 mL volumetric flask. If disposable glassware is preferred, the 20 mL scintillation vial may be calibrated for use. Pipet 10.0 mL of extraction solvent into the scintillation vial and mark the bottom of the meniscus. Discard this solvent.

7.3 Transfer approximately 1 g of each phase of the sample to separate 20 mL vials or 10 mL volumetric flasks (record weight to the nearest 0.1 g). Wipe the mouth of the vial with a tissue to remove any sample material. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

7.4 Add 2.0 mL surrogate spiking solution to all samples and blanks. For the sample in each analytical batch selected for spiking, add 2.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 200 ng/µL of each base/neutral analyte and 400 ng/µL of each acid analyte in the extract to be analyzed (assuming a 1 µL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column. See Method 3500 and the determinative method to be used for details on the surrogate standard and matrix spiking solutions.

7.5 Immediately dilute to 10 mL with the appropriate solvent. For compounds to be analyzed by GC/ECD, e.g., organochlorine pesticides and PCBs, the dilution solvent should be hexane. For base/neutral and acid semivolatile priority pollutants, use methylene chloride. If the dilution is to be cleaned up by gel permeation chromatography (Method 3640), use methylene chloride as the dilution solvent for all compounds.

7.6 Add 2.0 g of anhydrous sodium sulfate to the sample.

7.7 Cap and shake the sample for 2 min.

7.8 Loosely pack disposable Pasteur pipets with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect 5 mL of the extract in a tube or vial.

7.9 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

8.0 QUALITY CONTROL

8.1 Any reagent blanks and matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

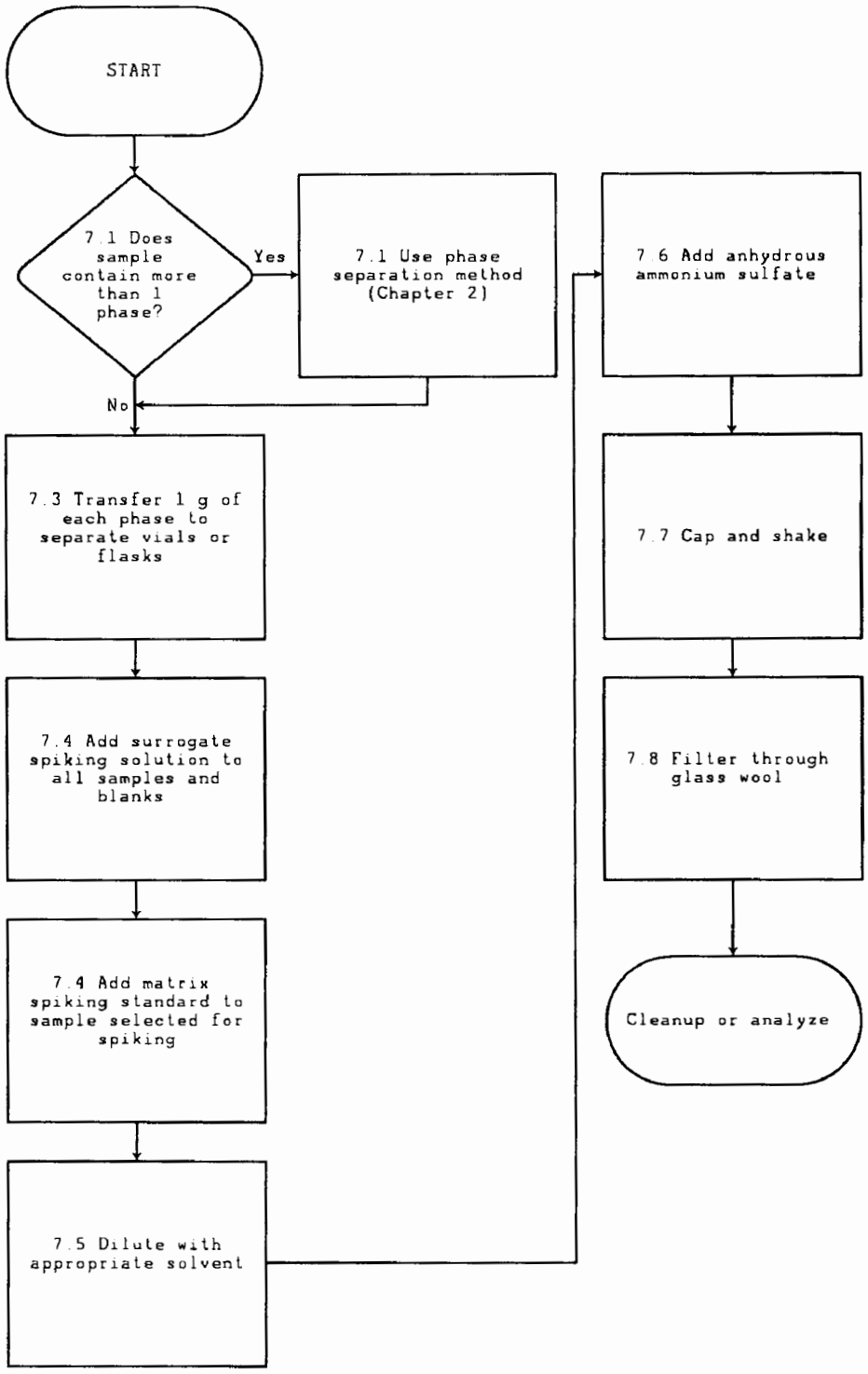
8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

10.1 None applicable.


START
7.1 Does sample contain more than 1 phase?
Yes
No
7.1 Use phase separation method (Chapter 2)
7.3 Transfer 1 g of each phase to separate vials or flasks
7.4 Add surrogate spiking solution to all samples and blanks
7.4 Add matrix spiking standard to sample selected for spiking
7.5 Dilute with appropriate solvent
7.6 Add anhydrous ammonium sulfate
7.7 Cap and shake
7.8 Filter through glass wool
Cleanup or analyze

METHOD 3585

WASTE DILUTION FOR VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 This method describes a solvent dilution of a non-aqueous waste sample prior to direct injection analysis. It is designed for use in conjunction with GC or GC/MS analysis of wastes that may contain organic chemicals at a concentration greater than 1 mg/kg and that are soluble in the dilution solvent. Method 3585 has adequate sensitivity to determine the regulatory concentrations of the Toxicity Characteristic (TC) Rule.

1.2 This method may be used with *n*-hexadecane for direct injection of target volatiles in oily matrices.

1.3 Use of a 1 - 2 µL injection of a 1:1 dilution can be used to provide detection limits of 0.5 ppm for volatile target analytes with a sensitive GC/MS.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Highly contaminated or highly complex samples may be diluted prior to analysis for volatiles using direct injection.

2.2 One gram of sample is weighed into a capped tube or volumetric flask. The sample is diluted to 2.0 - 10.0 mL with *n*-hexadecane or other appropriate solvent.

2.3 Diluted samples are injected into the GC or GC/MS for analysis.

3.0 INTERFERENCES

3.1 Use of a direct injection procedure will result in considerable contamination of injection ports, injection port liners, GC columns, and detectors. A Pyrex® wool plug should be placed into the injection port liner and the liner should be changed after every 12 hours of sample analysis.

3.2 The solvent used for waste dilution may contain volatile contaminants that could interfere with analyses.

3.2.1 *n*-Hexadecane elutes after target volatiles. However, volatile impurities in n-hexadecane may interfere with analyses.

3.2.2 Each lot of *n*-hexadecane (or any other solvent used for dilution) must be analyzed for impurities prior to use.

3.3 The presence of methanol and other oxygenated solvents in samples may lead to baseline humps that interfere with qualitative and quantitative analysis of early eluting target analytes when direct injection is employed.

4.0 APPARATUS AND MATERIALS

4.1 Glass scintillation vials - At least 20-mL, with polytetrafluoroethylene (PTFE)- or aluminum foil-lined screw-cap, or equivalent.

4.2 Spatula - Stainless steel or PTFE.

4.3 Balance - Capable of weighing 100 g to the nearest 0.01 g.

4.4 Vials and caps - 2-mL, for GC autosampler.

4.5 Disposable pipets - Pasteur.

4.6 Test tube rack.

4.7 Pyrex® glass wool.

4.8 Volumetric flasks, Class A - 2- or 10-mL (optional).

4.9 Direct injection liner (HP catalogue #18740-80200 or equivalent) - Modify with a 1-cm plug of Pyrex® wool placed approximately 50-60 mm down the length of the injection port (towards the oven). A 0.53 mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications. Figure 1 is an example of the placement of the glass wool plug in the liner.

mm

Figure 1 Modified Injector

5.0 REAGENTS

n-Hexadecane, *n*-$C_{16}H_{34}$ - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Samples consisting of multiple phases must be prepared by the phase separation method (Chapter Two) before extraction. The oil phase is prepared as outlined below. An aqueous phase is prepared and analyzed following the guidance in Method 5030.

7.2 The sample dilution may be performed in a 2- or 10-mL volumetric flask. If disposable glassware is preferred, the 10-dram vial may be calibrated for use. Pipet 2.0 mL of methanol into the vial and mark the bottom of the meniscus. Discard this solvent. Dry the vial.

7.3 Transfer approximately 1 g of the oil phase of the sample to a vial or volumetric flask (record weight to the nearest 0.1 g). Wipe the mouth of the vial with a tissue to remove any sample material. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

7.4 Immediately dilute to volume with *n*-hexadecane or other appropriate solvent. The choice of solvents is dependent on the nature of the target analytes. *n*-Hexadecane is late eluting and, therefore, presents no solvent interference for the majority of volatile organics. An early eluting solvent, e.g., pentane or hexane, may be chosen if the target analytes are mid to late eluting.

7.5 Add surrogate spiking solution, if required, for the analytical method to be employed.

7.6 Cap and shake the sample for 2 minutes.

7.7 The extract is ready for analysis by GC Methods 8015 or 8021, or by GC/MS Method 8260.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One, Method 8000, and the analytical method to be employed, for specific quality control procedures.

8.2 Each time samples are prepared and analyzed, and when there is a change in reagents, a reagent blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. Any reagent blanks, matrix spike samples, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Each analysis batch of 20 or fewer samples must contain: a reagent blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis; and a laboratory control sample, unless the determinative method provides other guidance.

8.4 Surrogates should be added to all samples when specified in the appropriate determinative method.

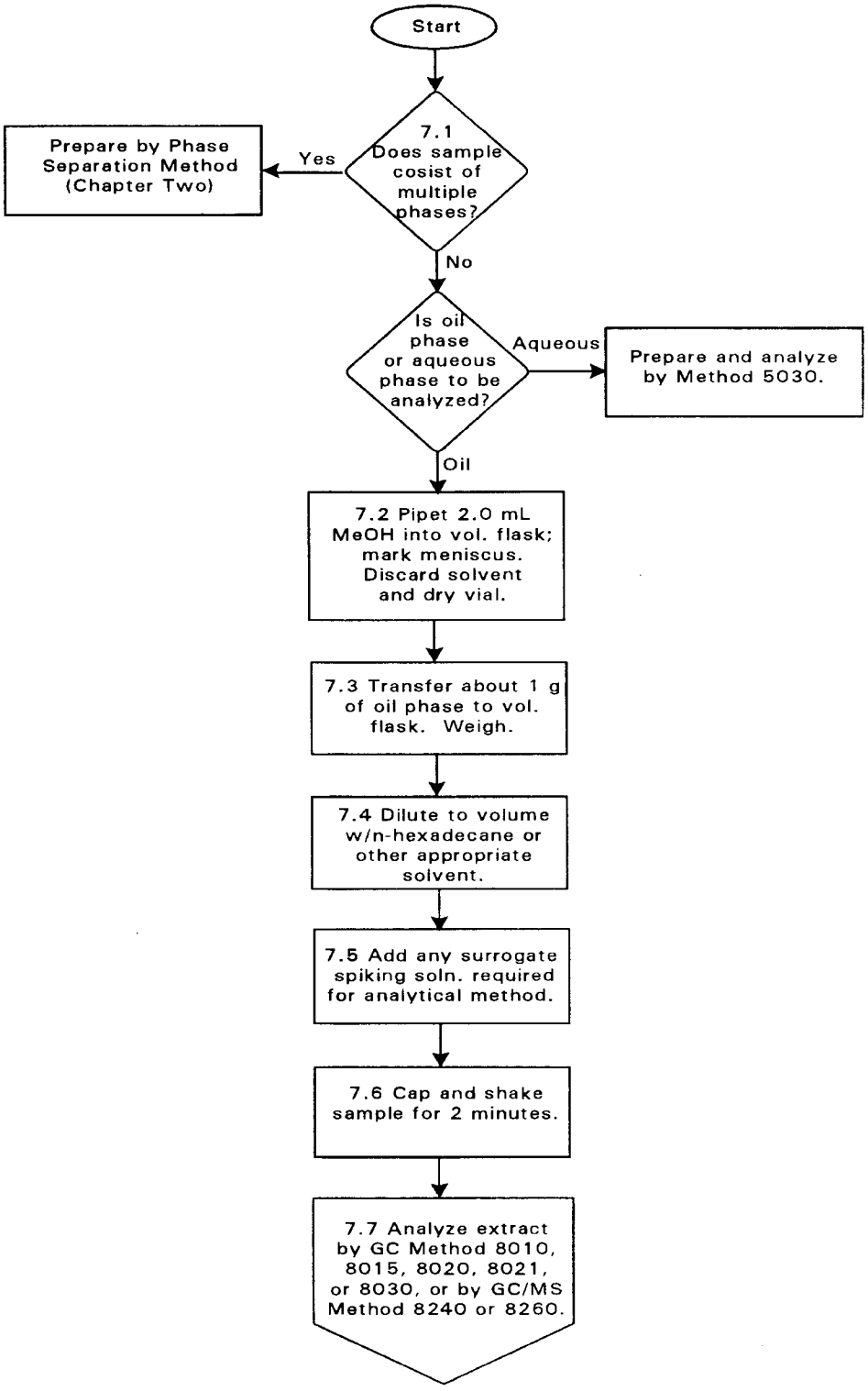
9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

1. Marsden, P.J., Colby, B.N., and Helms, C.L., "Determining TCLP Volatiles at Regulatory Levels in Waste Oil", Proceedings of the Eighth Annual Waste Testing and Quality Assurance Symposium, July, 1992.

WASTE DILUTION FOR VOLATILE ORGANICS



METHOD 3600C

CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3600 provides general guidance on selection of cleanup methods that are appropriate for the target analytes of interest. Cleanup methods are applied to the extracts prepared by one of the extraction methods, to eliminate sample interferences.

1.2 The following table lists the cleanup methods and provides a brief description of the type of cleanup.

Method No.	Method Name	Cleanup Type
3610	Alumina Cleanup	Adsorption
3611	Alumina Cleanup and Separation of Petroleum Wastes	Adsorption
3620	Florisil Cleanup	Adsorption
3630	Silica Gel Cleanup	Adsorption
3640	Gel-Permeation Cleanup (GPC)	Size-Separation
3650	Acid-Base Partition Cleanup	Acid-Base Partitioning
3660	Sulfur Cleanup	Oxidation/Reduction
3665	Sulfuric Acid/Permanganate Cleanup	Oxidation/Reduction

1.3 The purpose of applying a cleanup method to an extract is to remove interferences and high boiling material that may result in:

- errors in quantitation (data may be biased low because of analyte adsorption in the injection port or front of the GC column or biased high because of overlap with an interference peak);
- false positives because of interference peaks falling within the analyte retention time window;
- false negatives caused by shifting the analyte outside the retention time window;
- rapid deterioration of expensive capillary columns; and,
- instrument downtime caused by cleaning and rebuilding of detectors and ion sources.

1.4 The following techniques have been applied to extract purification: adsorption chromatography; partitioning between immiscible solvents; gel permeation chromatography; oxidation of interfering substances with acid, alkali, or oxidizing agents. These techniques may be used individually or in various combinations, depending on the extent and nature of the co-extractives.

1.5 Most extracts of soil and waste require some degree of cleanup, whereas, cleanup for water extracts may be unnecessary. Highly contaminated extracts (e.g. sample extracts of oily waste or soil containing oily residue) often require a combination of cleanup methods. For example, when analyzing for organochlorine pesticides and PCBs, it may be necessary to use gel permeation

chromatography (GPC), to eliminate the high boiling material and a micro alumina or Florisil column to eliminate interferences with the analyte peaks on the GC/ECD.

1.6 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

2.0 SUMMARY OF METHOD

Refer to the specific cleanup method for a summary of the procedure.

3.0 INTERFERENCES

3.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by running laboratory reagent blanks.

3.2 More extensive procedures than those outlined in the methods may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

Refer to the specific cleanup method for apparatus and materials needed.

5.0 REAGENTS

Refer to the specific cleanup method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples normally undergo solvent extraction. Chapter Two, Sec. 2.0, may be used as a guide for choosing the appropriate extraction procedure based on the physical composition of the waste and on the analytes of interest in the matrix (see also Method 3500 for a general description of the extraction technique). For some organic liquids, extraction prior to cleanup may not be necessary.

7.2 Most soil/sediment and waste sample extracts will require some degree of cleanup. The extract is then analyzed by one of the determinative methods. If interferences still preclude analysis for the analytes of interest, additional cleanup may be required.

7.3 Many of the determinative methods identify cleanup methods that should be used when determining particular analytes (e.g., Method 8061, gas chromatography of phthalate esters, recommends using either Method 3610 (alumina column cleanup) or Method 3620 (Florisil column cleanup) if interferences prevent analysis. However, the experience of the analyst may prove invaluable in determining which cleanup methods are needed. Many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations, however, each cleanup step has the potential to decrease the analytical sensitivity through small losses of analytes during the cleanup. As a result, when multiple cleanup procedures are necessary, additional care is recommended to mnimize analyte loss during each individual cleanup procedure.

7.4 Specific guidance on each cleanup technique is listed in the individual cleanup methods that follow. The amount of extract cleanup required prior to the final determination depends on the concentration of interferences in the sample, the selectivity of both the extraction procedure and the determinative method and the required detection limit. The following Sections give a description of the different cleanup approaches:

7.4.1 Adsorption chromatography - Alumina (Methods 3610 and 3611), Florisil (Method 3620), and silica gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity. These are primarily used for cleanup of a specific chemical group of relatively non-polar analytes, i.e., organochlorine pesticides, polynuclear aromatic hydrocarbons (PAHs), nitrosamines, etc.. Solid phase extraction cartridges have been added as an option.

7.4.2 Acid-base partitioning (Method 3650) - Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols. It is very useful for separating the neutral PAHs from the acidic phenols when analyzing a site contaminated with creosote and pentachlorophenol.

7.4.3 Gel permeation chromatography (GPC) (Method 3640) - The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight, high boiling material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Target Compound list prior to GC/MS analysis for semivolatiles and pesticides. GPC may not be applicable to elimination of extraneous peaks on a chromatogram which interfere with the analytes of interest. It is, however, useful for the removal of high boiling materials which would contaminate injection ports and column heads, prolonging column life, stabilizing the instrument, and reducing column reactivity.

7.4.4 Sulfur cleanup (Method 3660) - Useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.

7.4.5 Sulfuric acid/permanganate cleanup (Method 3665) - Useful for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls (PCBs). This method should be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

7.5 Fractionation is a useful technique that can aid in the separation of complex mixtures of analytes. For instance, an analyst may use Method 3630 (Silica Gel) for separating the PCBs away from most organochlorine pesticides. Method 3611 (Alumina) may be used for fractionation of aliphatic, aromatic, and polar analytes. Method 3620 (Florisil) provides for fractionation of the organochlorine pesticides.

7.6 Cleanup capacity is another factor that must be considered in choosing a cleanup technique. The adsorption methods (3610, 3620, and 3630) provide the option of using standard column chromatography techniques or solid phase extraction cartridges. The decision process in selecting between the different options available generally depends on the amount of interferences/high boiling material in the sample extract and the degree of cleanup required by the determinative method. The solid phase extraction cartridges require less elution solvent and less time, however, their cleanup capacity is drastically reduced when comparing a 0.5 g or 1.0 g Florisil cartridge to a 20 g standard Florisil column. The same factor enters into the choice of the 70 g gel permeation column specified in Method 3640 versus a high efficiency column. As with any other method choice issue, the responsibility for ensuring that the use of a cartridge cleanup is appropriate lies with the laboratory. If the results from a sample analysis suggest that the cleanup was not effective because the capacity of the cartridge was exceeded, then it may be necessary to repeat the procedures with either a larger cartridge or the standard column chromatographic procedure.

7.7 Table 1 indicates the recommended cleanup techniques for the indicated groups of compounds. This information can also be used as guidance for compounds that are not listed. Compounds that are chemically similar to these groups of compounds should behave similarly when taken through the cleanup procedure. However, this must be demonstrated by determining recovery of standards taken through the method.

7.8 Following cleanup, the sample is concentrated to whatever volume is listed in the determinative method using the procedures described in the appropriate 3500 series method. Analysis follows as per the appropriate determinative procedure.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples. For sample extracts that are cleaned up, the associated quality control samples (e.g. spikes, blanks, replicates, and duplicates) must also be processed through the same cleanup procedure.

8.3 The analysis using each determinative method (GC, GC/MS, HPLC) lists instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

9.0 METHOD PERFORMANCE

Refer to the specific cleanup method for performance data.

10.0 REFERENCES

Refer to the specific cleanup method.

TABLE 1.

RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

Analyte Group	Determinative[a] Method	Cleanup Method Options
Phenols	8041	3630[b], 3640, 3650, 8041[c]
Phthalate esters	8061	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides	8081	3620, 3640, 3660
PCBs	8082	3620, 3630, 3665
Nitroaromatics and cyclic ketones	8091	3620, 3640
Polynuclear aromatic hydrocarbons	8100/8310	3611, 3630, 3640
Haloethers	8111	3620, 3640
Chlorinated hydrocarbons	8121	3620, 3640
Aniline and derivatives	8131	3620, 3640
Organophosphorus pesticides	8141	3620
Chlorinated herbicides	8151	8151[d], 3620
Semivolatile organics	8270	3640, 3650, 3660
Petroleum waste	8270	3611, 3650
PCDDs and PCDFs by LR/MS	8280	8280
PCDDs and PCDFs by HR/MS	8290	8290
N-methyl carbamate pesticides	8318	8318

[a] The GC/MS Method 8270 is also an appropriate determinative method for all analyte groups, unless lower detection limits are required.

[b] Cleanup applicable to derivatized phenols.

[c] Method 8041 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

[d] Method 8151 incorporates an acid-base cleanup step as an integral part of the method.

METHOD 3610B

ALUMINA CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic) for use in chromatographic cleanup procedures. It is used to separate analytes from interfering compounds of a different chemical polarity.

1.2 Each of the three pH ranges of alumina has different uses and disadvantages as a cleanup procedure.

1.2.1 Basic alumina has a pH of 9-10. It is used to separate basic and neutral compounds that are stable to alkali, alcohols, hydrocarbons, steroids, alkaloids, natural pigments. Its disadvantages are that it can cause polymerization, condensation, and dehydration reactions, and one cannot use acetone or ethyl acetate as eluants.

1.2.2 Neutral alumina has a pH of 6-8. It is used to separate aldehydes, ketones, quinones, esters, lactones, glycoside. Its disadvantage is that is it considerably less active than the basic form.

1.2.3 Acidic alumina has a pH of 4-5. It is used to separate acidic pigments (natural and synthetic), and strong acids (that otherwise chemisorb to neutral and basic alumina). This method does not address the use of acid alumina.

1.3 Basic, neutral, and acidic alumina can be prepared in various activity grades (I to V), based on the Brockmann scale reproduced below. Grade I is prepared by heating alumina until no more water is lost (typically overnight at 400-450°C, but other time-temperature relationships may be employed). The other grades (II-V) are prepared by adding water to Grade I to deactivate it.

Activity grade	I	II	III	IV	V
Water added (wt. %)	0	3	6	10	15
RF (p-aminoazobenzene)	0.0	0.13	0.25	0.45	0.55

where RF is the retention factor for p-aminoazobenzene.

1.4 Alumina cleanup may be accomplished using a glass chromatographic column packed with alumina or using solid-phase extraction cartridges containing alumina.

1.5 This method includes procedures for cleanup of sample extracts containing phthalate esters and nitrosamines. See Method 3611, Alumina Column Cleanup of Petroleum Wastes, for alumina cleanup of petroleum wastes.

1.6 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method describes procedures for alumina cleanup of solvent extracts of environmental samples. It provides the option of using either traditional column chromatography techniques or solid-phase extraction cartridges. Generally, the traditional column chromatography technique uses larger amounts of adsorbent and, therefore, has a greater cleanup capacity.

2.2 In the column cleanup protocol, the column is packed with the appropriate amount of adsorbent, topped with a water adsorbent, and then loaded with the sample extract. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate may be further concentrated prior to gas chromatographic analysis.

2.3 The cartridge cleanup procedure uses solid-phase extraction cartridges containing 40 µm particles of alumina (60 Å pores). Each cartridge is washed with solvent immediately prior to use. The sample extract is loaded onto the cartridge which is then eluted with suitable solvent(s). A vacuum manifold is needed to obtain reproducible results. The eluate may be further concentrated prior to gas chromatographic analysis.

2.4 The phthalate esters may be considered either the analytes of interest or the interferants, depending on which eluant fraction is analyzed.

3.0 INTERFERENCES

3.1 A reagent blank should be prepared and analyzed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 The procedures for reagent purification outlined here should be considered to be the minimum requirements for use of this method. More extensive procedures may be necessary to achieve acceptable levels of interferences for some analytes.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column - 300 mm x 10 mm ID, with a polytetrafluoroethylene (PTFE) stopcock.

NOTE: Columns with fritted glass discs are difficult to clean once the column has been used to process highly contaminated extracts. Columns without frits may be purchased, and a small pad of Pyrex® glass wool may be used to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers - Appropriates sizes

4.3 Reagent bottle - Appropriate sizes

4.4 Muffle furnace - capable of maintaining 400°C.

4.5 Vials - Glass, 2-mL capacity, with PTFE-lined screw caps or crimp tops.

4.6 Vacuum manifold - VacElute Manifold SPS-24 (Analytichem International), Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500-mL sidearm flask fitted with a one-hole stopper and glass tubing. The manifold is needed for use of the cartridge cleanup protocol.

4.7 Top-loading balance - capable of weighing 0.01 g.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Sodium sulfate - Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. A method blank must be analyzed in order to demonstrate that there is no interference from the sodium sulfate.

5.3 Eluting solvents - all solvents must be pesticide quality or equivalent.

5.3.1 Diethyl Ether, $C_2H_5OC_2H_5$. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.3.2 Methanol, CH_3OH

5.3.3 Pentane, $CH_3(CH_2)_3CH_3$

5.3.4 Hexane, C_6H_{14}

5.3.5 Methylene chloride, CH_2Cl_2

5.3.6 Acetone, CH_3COCH_3

5.4 Granular alumina, for column cleanup procedure

5.4.1 Neutral alumina, for cleanup of phthalates, activity Super I, W200 series (ICN Life Sciences Group, No. 404583 or equivalent). To activate, place 100 g of alumina into a 500-mL beaker and heat for approximately 16 hr at 400°C. After heating, transfer to a 500-mL reagent bottle. Tightly seal the bottle and cool to room temperature. When cool, add 3 mL of organic-free reagent water. Mix thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. The preparation should be homogeneous before use. Keep the bottle sealed tightly to ensure proper activity. Super I alumina cited above is a Grade I reagent with a very high binding capacity. The neutral alumina employed in this method may be prepared from reagents other than Super I, provided that adequate performance can be demonstrated.

5.4.2 Basic alumina, for cleanup of nitrosamines, activity Super I, W200 series (ICN Life Sciences Group, No. 404571, or equivalent). To activate, place 100 g of alumina into a 500-mL reagent bottle and add 2 mL of organic-free reagent water. Mix thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. The preparation should be homogeneous

before use. Keep the bottle sealed tightly to ensure proper activity. Super I alumina cited above is a Grade I reagent with a very high binding capacity. The basic alumina employed in this method may be prepared from reagents other than Super I, provided that adequate performance can be demonstrated.

5.5 Alumina cartridges - 40 µm particles, 60 Å pores, for cleanup of phthalates. The cartridges from which this method were developed consist of 6-mL serological-grade polypropylene tubes, with the 1 g of alumina held between two polyethylene or stainless steel frits with 20 µm pores. Cartridges containing 0.5 g and 2.0 g of alumina are available, however, the compound elution patterns need to be verified when cartridges containing other than 1 g of alumina are used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

The chromatographic separation procedures for the phthalate esters may be accomplished by either the column cleanup approach (Sec. 7.3) or the cartridge cleanup approach (Sec. 7.4). The procedure for the nitrosamines includes only the column cleanup approach (Sec. 7.5). Sec. 7.1 describes the procedures for assembling and conditioning the alumina cartridges. Sec. 7.2 describes general procedures for handling sample extracts prior to cleanup.

The column chromatography procedures employ a larger amount of alumina than the cartridge procedures and, therefore, have a greater cleanup capacity. Samples that exhibit greater degrees of interferences should be cleaned up using the column procedures. However, both techniques have limitations on the amount of interferences that they can remove.

7.1 Cartridge set-up and conditioning

7.1.1 Arrange the cartridges on the manifold in the closed-valve position.

7.1.2 Turn on the vacuum pump and set the vacuum to 10 in (254 mm) of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates may be controlled by opening and closing cartridge valves.

7.1.3 Condition the cartridges by adding 4 mL of hexane to each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes. Do not turn off the vacuum.

7.1.4 Slowly open cartridge valves to allow the hexane to pass through the cartridges. Close the cartridge valves when there is still at least 1 mm of solvent above the sorbent bed. Do not allow cartridges to become dry. If cartridges go dry, repeat the conditioning step.

7.2 Handling sample extracts

7.2.1 Reduce the sample extract volume to 2 mL (per 3500 series methods) prior to cleanup. The extract solvent should be hexane for the phthalate esters and methylene chloride for the nitrosamines.

7.2.2 Allow extract to reach room temperature if it was in cold storage. Inspect the extract visually to ensure that there are no particulates or phase separations and that no evaporative loss has taken place. If crystals of sulfur are visible or if the presence of sulfur is suspected, proceed with Method 3660.

7.3 Column procedure for phthalate esters

7.3.1 Place approximately 10 g of neutral alumina (Sec. 5.4.1) into a 10-mm ID chromatographic column. Tap the column to settle the alumina, and add 1-2 cm of anhydrous sodium sulfate to the top.

7.3.2 Pre-elute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract (Sec. 7.2) onto the column using an additional 2 mL of hexane to complete the transfer.

7.3.3 Just prior to exposure of the sodium sulfate layer to the air, add 35 mL of hexane to the column and continue the elution of the column. Discard this hexane eluate.

7.3.4 Elute the column with 140 mL of ethyl ether/hexane (20/80, v/v) and collect this fraction in a flask for concentration.

7.3.5 Concentrate the collected fraction to the volume required by the determinative method (e.g., 2 mL for Method 8061), using the techniques described in the appropriate 3500 series method. No solvent exchange is necessary. Compounds that elute in this fraction are:

Bis(2-ethylhexyl) phthalate	Diethyl phthalate
Butyl benzyl phthalate	Dimethyl phthalate
Di-n-butyl phthalate	Di-n-octyl phthalate

7.4 Cartridge procedure for phthalate esters

NOTE: If organochlorine pesticides are known to be present in the extract, Florisil cartridges (Method 3620) are recommended instead of Alumina cartridges.

7.4.1 Using 1-g alumina cartridges, condition the cartridges with hexane as described in Sec. 7.1.

7.4.2 Transfer the extract (Sec. 7.2) to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.4.3 When the entire extract has passed through the cartridge, but before the cartridge becomes dry, rinse the sample vial with an additional 0.5 mL of solvent, and add the rinse to the cartridge to complete the quantitative transfer.

7.4.4 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never gets dry.

7.4.5 Place a 5-mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align it with the collection vial.

7.4.6 Add 10 mL of acetone/hexane (20/80, v/v) to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 in (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial.

7.4.7 Adjust the final volume of the eluant to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.5 Column procedure for nitrosamines

7.5.1 Diphenylamine, if present in the original sample extract, must be separated from the nitrosamines if N-nitrosodiphenylamine is to be determined by this method.

7.5.2 Place approximately 12 g of basic alumina (Sec. 5.4.2) into a 10-mm ID chromatographic column. Tap the column to settle the alumina and add 1-2 cm of anhydrous sodium sulfate to the top.

7.5.3 Pre-elute the column with 10 mL of ethyl ether/pentane (30/70, v/v). Discard the eluate (about 2 mL) and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract (Sec. 7.2, in methylene chloride) onto the column using an additional 2 mL of pentane to complete the transfer.

7.5.4 Just prior to exposure of the sodium sulfate layer to the air, add 70 mL of ethyl ether/pentane (30/70, v/v). Discard the first 10 mL of eluate. Collect the remainder of the eluate in a flask for concentration.

This fraction contains some N-nitroso-di-n-propylamine, if any is present in the sample extract.

7.5.5 Elute the column with 60 mL of ethyl ether/pentane (50/50, v/v), collecting the eluate in a second flask for concentration. Add 15 mL of methanol to the flask.

This fraction will contain N-nitrosodimethylamine, most of the N-nitroso-di-n-propylamine, and any diphenylamine that is present.

7.5.6 Concentrate both fractions to the final volumes listed in the appropriate determinative method, using the techniques described in the appropriate 3500 series method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst must demonstrate that the compounds of interest are quantitatively (70-130%) recovered before applying this method to actual samples. This test applies to both the column cleanup and cartridge cleanup procedures. A recovery check needs to be performed using standards of the target analytes at a known concentration near the regulatory limit or action level for the target analyte.

8.2.1 This test should be conducted on each batch of alumina following its activation (Sec. 5.4).

8.2.2 The efficiency of each lot of the solid-phase extraction cartridges needs to be verified. Only lots of cartridges from which the spiked analytes are quantitatively recovered may be used to process the samples. A check should also be performed at least once on each individual lot of cartridges and at least once for every 300 cartridges of a particular lot, whichever frequency is greater.

8.3 The quality control samples associated with sample extracts that are cleaned up using this method, should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

Table 1 provides data for the recoveries of phthalate esters obtained from 1-g alumina cartridges.

10.0 REFERENCES

1. U.S. EPA, "Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges", Project Report, December 1989.

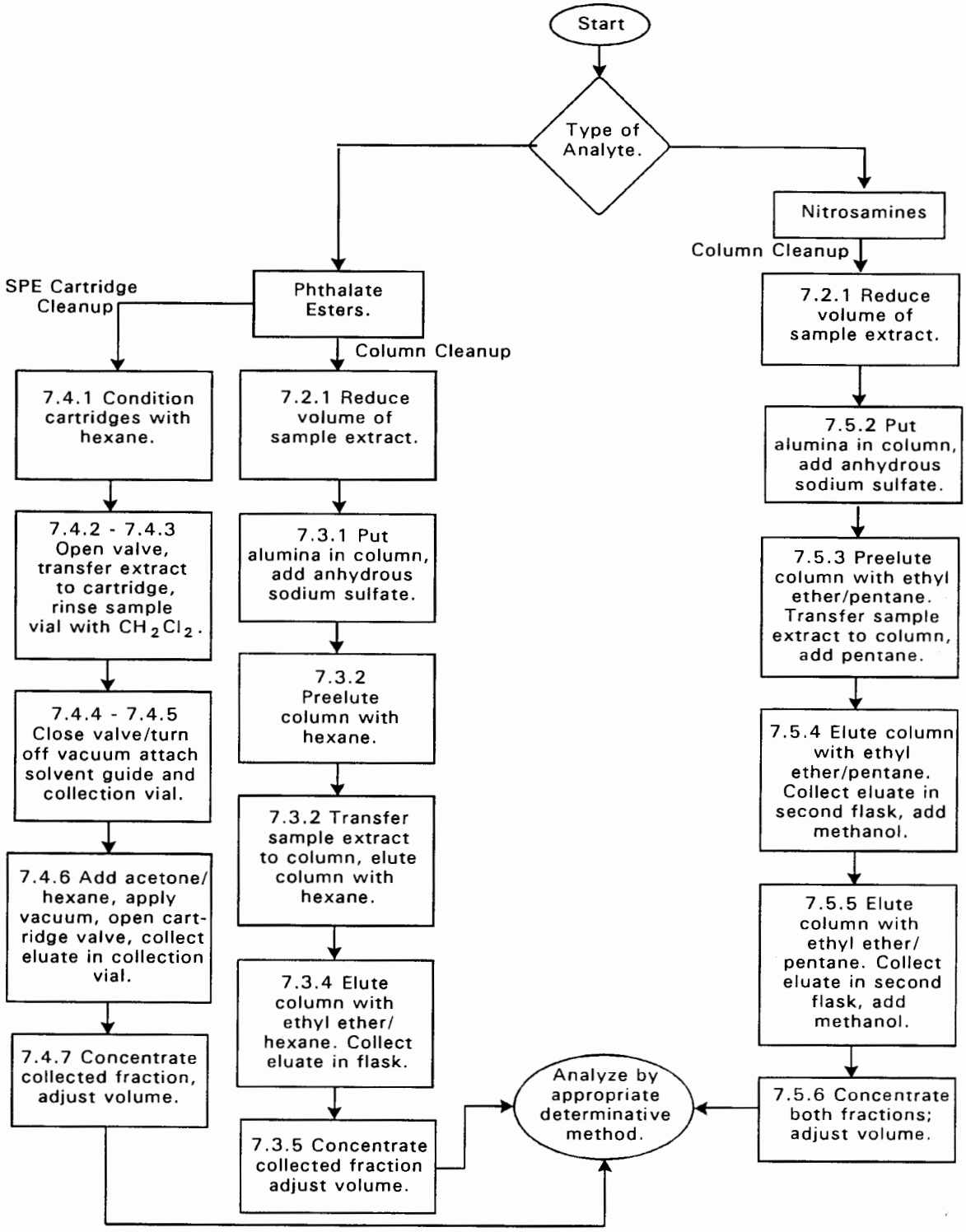
TABLE 1

PERCENT RECOVERIES AND ELUTION PATTERNS FOR
16 PHTHALATE ESTERS FROM ALUMINA CARTRIDGES[a]

Compound	Average % Recovery	Average RSD
Dimethyl phthalate	108	4.6
Diethyl phthalate	129	6.6
Diisobutyl phthalate	92.6	7.3
Di-n-butyl phthalate	107	5.6
Bis(4-methyl-2-pentyl) phthalate	88.3	9.8
Bis(2-methoxyethyl) phthalate	92.2	5.0
Diamyl phthalate	100	6.4
Bis(2-ethoxyethyl) phthalate	101	6.3
Hexyl 2-ethylhexyl phthalate	93.2	13
Dihexyl phthalate	113	5.4
Benzyl butyl phthalate	104	3.9
Bis(2-n-butoxyethyl) phthalate	99.5	4.7
Bis(2-ethylhexyl) phthalate	101	6.1
Dicyclohexyl phthalate	97.2	6.2
Di-n-octyl phthalate	103	7.5
Dinonyl phthalate	110	5.2

[a] Alumina cartridges (J.T. Baker) were conditioned with 4 mL of hexane. Each experiment was performed in duplicate at three spiking concentrations (40 µg, 80 µg, and 120 µg per compound, per cartridge). The cartridges were eluted with 5 mL of acetone/hexane (20/80, v/v).

ALUMINA CLEANUP



METHOD 3611B

ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES

1.0 SCOPE AND APPLICATION

1.1 Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic) for use in chromatographic cleanup procedures. Method 3611 utilizes neutral pH alumina to separate petroleum wastes into aliphatic, aromatic, and polar fractions.

1.2 Method 3611 was formerly Method 3570 in the Second Edition of this manual.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate is then concentrated (if necessary).

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Caution must be taken to prevent overloading of the chromatographic column. As the column loading for any of these types of wastes approaches 0.300 g of extractable organics, separation recoveries will suffer. If overloading is suspected, an aliquot of the base-neutral extract prior to cleanup may be weighed and then evaporated to dryness. A gravimetric determination on the aliquot will indicate the weight of extractable organics in the sample.

3.4 Mixtures of petroleum wastes containing predominantly polar solvents, i.e., chlorinated solvents or oxygenated solvents, are not appropriate for this method.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300 mm x 10 mm ID, with Pyrex® glass wool at bottom and a polytetrafluoroethylene (PTFE) stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the

glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: Appropriate sizes.

4.3 Reagent bottle: Appropriate sizes.

4.4 Muffle furnace.

4.5 Water bath: Heated with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Erlenmeyer flasks: 50 and 250 mL.

5.0 REAGENTS

5.1 Sodium sulfate: (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.2 Eluting solvents:

5.2.1 Methanol, CH_3OH - Pesticide quality or equivalent.

5.2.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.2.3 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.3 Alumina: Neutral 80-325 MCB chromatographic grade or equivalent. Dry alumina overnight at 130°C prior to use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 It is suggested that Method 3650, Acid-Base Partition Cleanup, be performed on the sample extract prior to alumina cleanup.

7.2 Place approximately 10 g of alumina into a chromatographic column, tap to settle the alumina, and add 1 cm of anhydrous sodium sulfate to the top.

7.3 Pre-elute the column with 50 mL of hexane. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 1 mL sample extract onto the column using an additional 1 mL of hexane to complete the transfer. To avoid overloading the column, it is suggested that no more than 0.300 g of extractable organics be placed on the column (see Sec. 3.3).

7.4 Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 1 mL of hexane was used as a rinse, then 13 mL of additional hexane should be used. Collect the effluent in a 50 mL flask and label this fraction "base/neutral aliphatics." Adjust the flow rate to 2 mL/min.

7.5 Elute the column with 100 mL of methylene chloride and collect the effluent in a 250 mL flask. Label this fraction "base/neutral aromatics."

7.6 Elute the column with 100 mL of methanol and collect the effluent in a 250 mL flask. Label this fraction "base/neutral polars."

7.7 Following cleanup, concentrate the fractions to the final volumes listed in the appropriate determinative method, using the techniques described in an appropriate 3500 series method. Analysis follows as specified in the determinative procedure.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

9.2 Rag oil is an emulsion consisting of crude oil, water, and soil particles. It has a density greater than crude oil and less than water. This material forms a layer between the crude oil and water when the crude oil is allowed to gravity separate at the refinery. A rag oil sample was analyzed by a number of laboratories according to the procedure outlined in this method. The results of these analyses by GC/MS for selected components in the rag oil are presented in Table 1. Reconstructed ion chromatograms from the GC/MS analyses are included as Figures 1 and 2.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1

RESULTS OF ANALYSIS FOR SELECTED COMPONENTS IN RAG OIL

Analyte	Mean Conc. (mg/kg)[a]	Standard Deviation	%RSD[b]
Naphthalene	216	42	19
Fluorene	140	66	47
Phenanthrene	614	296	18
2-Methylnaphthalene	673	120	18
Dibenzothiophene	1084	286	26
Methylphenanthrene	2908	2014	69
Methyldibenzothiophene	2200	1017	46
	Average Surrogate Recovery		
Nitrobenzene-d_5	58.6	11	
Terphenyl-d_{14}	83.0	2.6	
Phenol-d_6	80.5	27.6	
Naphthalene-d_8	64.5	5.0	

[a] Based on five determinations from three laboratories.

[b] Percent Relative Standard Deviation.

FIGURE 1

RECONSTRUCTED ION CHROMATOGRAM FROM GC/MS ANALYSIS OF THE AROMATIC FRACTION FROM RAG OIL

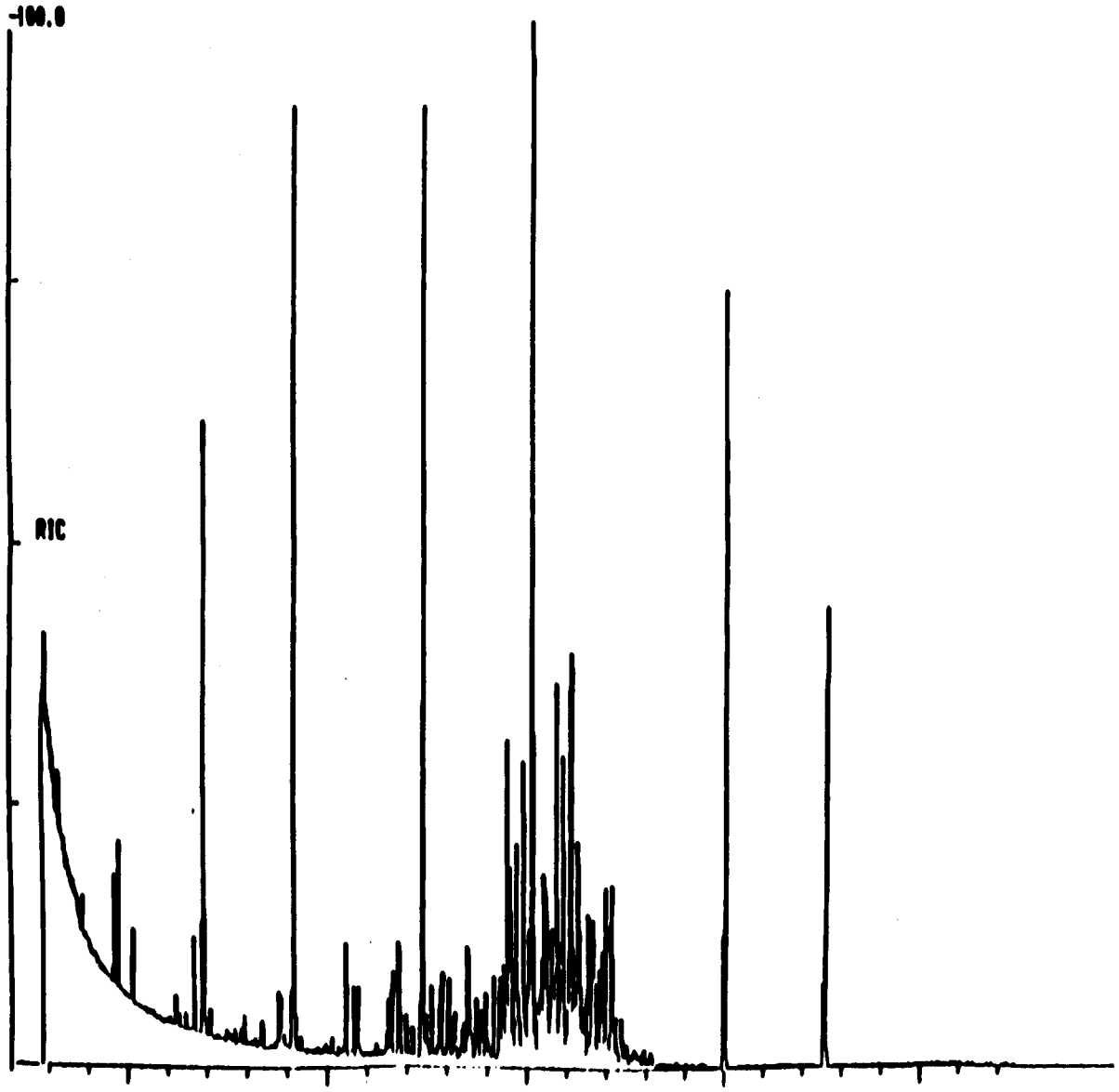
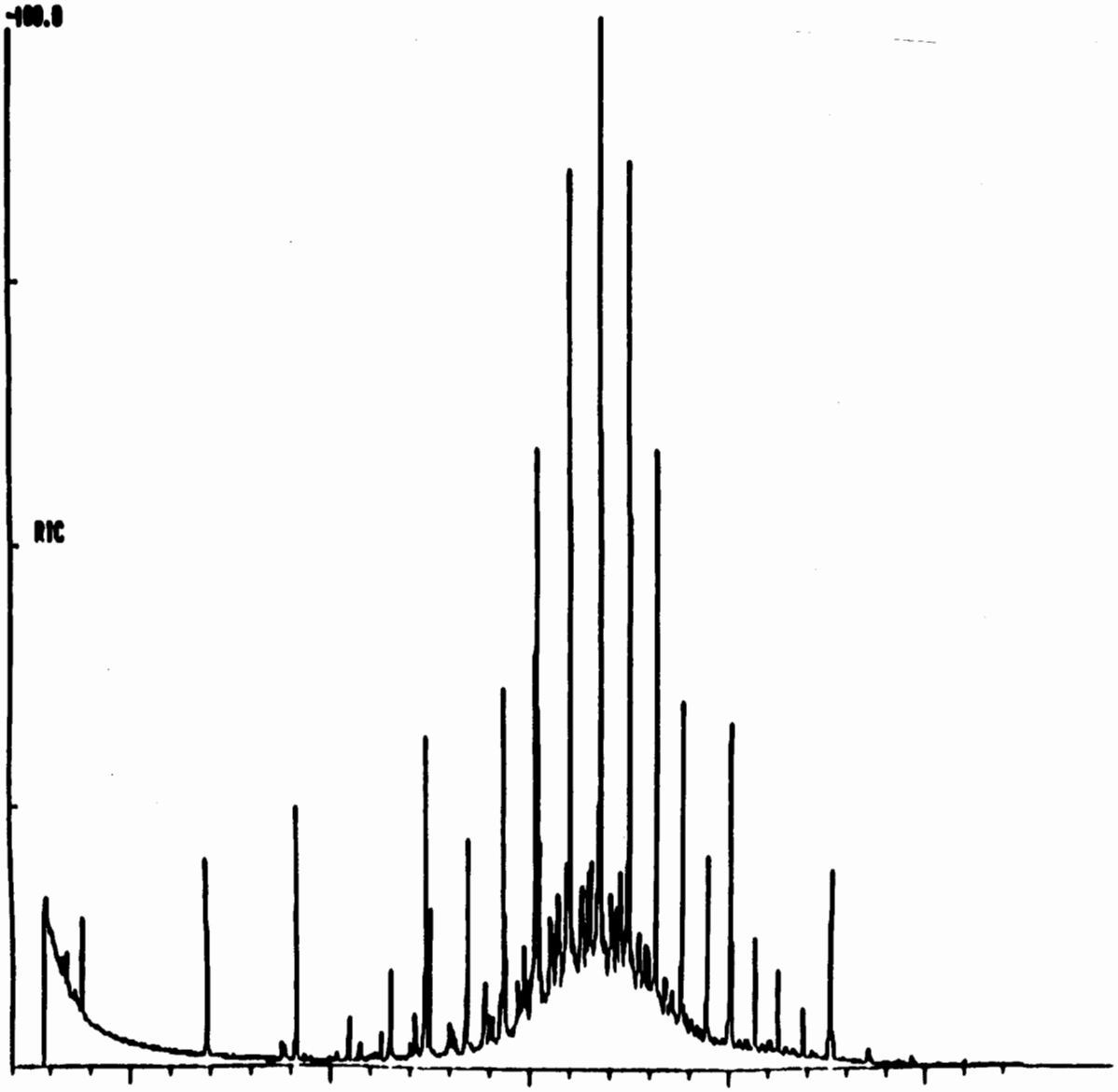
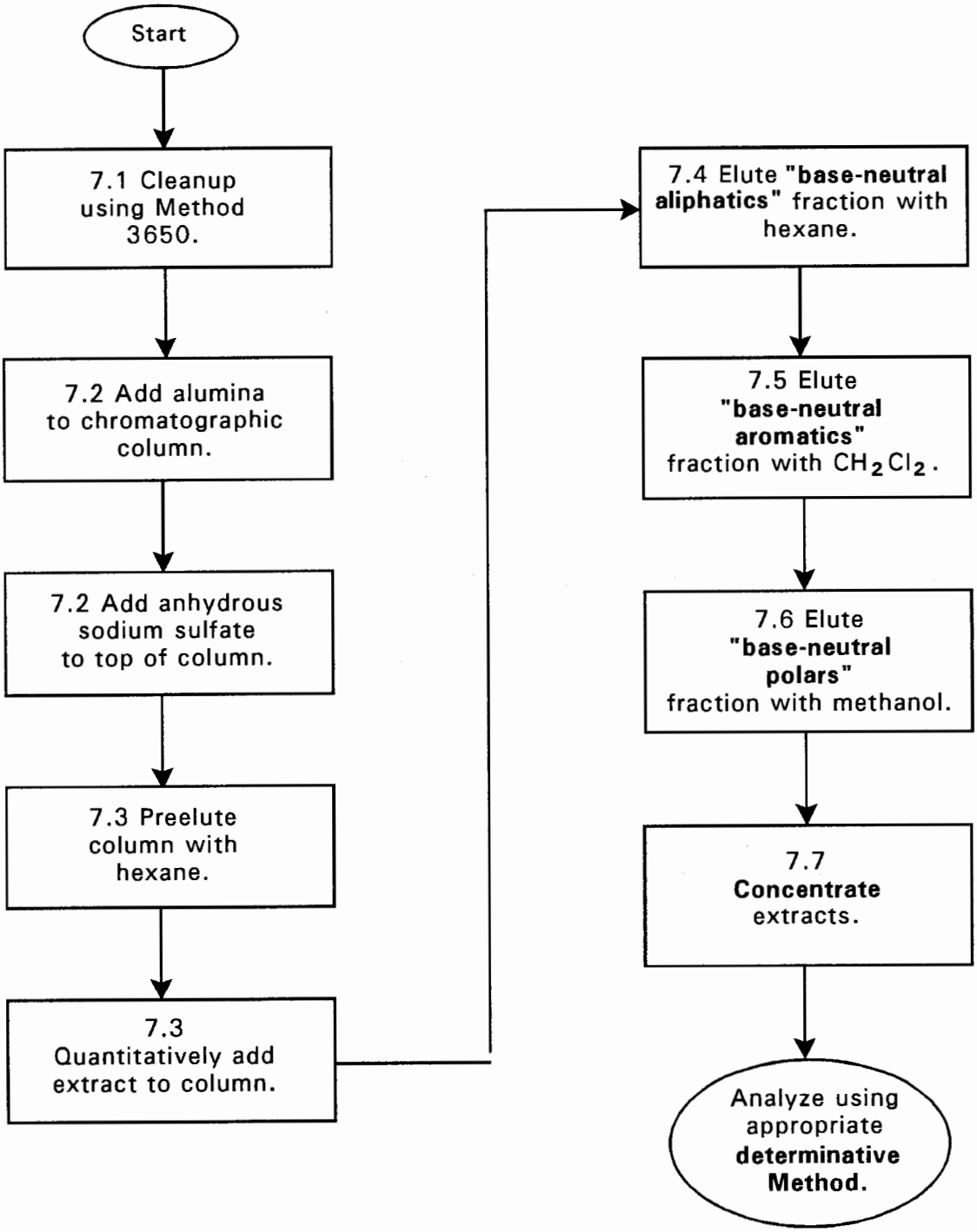


FIGURE 2

RECONSTRUCTED ION CHROMATOGRAM FROM GC/MS ANALYSIS OF THE ALIPHATIC FRACTION FROM RAG OIL



ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES



METHOD 3620B

FLORISIL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered trade name of U. S. Silica Co., is a magnesium silicate with basic properties. It is used to separate analytes from interfering compounds prior to sample analysis by a chromatographic method.

1.2 Florisil has been used for the cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes. Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates.

1.3 Florisil cleanup may be accomplished using a glass chromatographic column packed with Florisil or using solid-phase extraction cartridges containing Florisil.

1.4 This method includes procedures for cleanup of sample extracts containing the following analyte groups:

Phthalate esters	Chlorinated hydrocarbons
Nitrosamines	Organochlorine pesticides
Nitroaromatics	Organophosphates
Haloethers	Organophosphorus pesticides
Aniline and aniline derivatives	PCBs

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method describes procedures for Florisil cleanup of solvent extracts of environmental samples. It provides the option of using either traditional column chromatography techniques to solid-phase extraction cartridges. Generally, the traditional column chromatography technique uses larger amounts of adsorbent and, therefore, has a greater cleanup capacity.

2.2 In the column cleanup protocol, the column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample extract. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate may be further concentrated prior to gas chromatographic analysis.

2.3 The cartridge cleanup protocol uses solid-phase extraction cartridges containing 40 µm particles of Florisil (60 Å pores). Each cartridge is washed with solvent immediately prior to use. The sample extract is loaded onto the cartridge which is then eluted with suitable solvent(s). A vacuum manifold is required to obtain reproducible results. The eluate may be further concentrated prior to gas chromatographic analysis.

3.0 INTERFERENCES

3.1 A reagent blank should be prepared and analyzed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 The procedures for reagent purification outlined here should be considered to be the minimum requirements for use of this method. More extensive procedures may be necessary to achieve acceptable levels of interferences for some analytes. However, during the evaluation of the cartridge cleanup procedure, phthalate esters were detected in the Florisil cartridge method blanks at concentrations up to 400 ng per cartridge. Therefore, complete removal of the phthalate esters from Florisil cartridges may not be possible.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column - 300 mm x 10 mm ID, with a polytetrafluoroethylene (PTFE) stopcock.

NOTE: Columns with fritted glass discs are difficult to clean once the column has been used to process highly contaminated extracts. Columns without frits may be purchased, and a small pad of glass wool may be used to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers - Appropriate sizes.

4.3 Reagent bottle - Appropriate sizes.

4.4 Muffle furnace - capable of maintaining 400°C.

4.5 Vials - Glass, 10-mL and 25-mL capacity, with PTFE-lined screw caps or crimp tops.

4.6 Vacuum manifold - VacElute Manifold SPS-24 (Analytichem International), Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500-mL sidearm flask fitted with a one-hole stopper and glass tubing. The manifold is required for use of the cartridge cleanup protocol.

4.7 Top-loading balance - capable of weighing to 0.01 g.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Granular Florisil - for column cleanup procedure. Florisil is produced in four grades, two of which are appropriate for this procedure. The differences between grades are primarily a function

of the activation temperature, resulting in somewhat different chemical characteristics among the grades. Florisil PR is activated at 675°C and is most useful for pesticide residue analyses. Florisil A is activated at 650°C and is generally used for other analytes. Whichever grade is used, store Florisil in glass containers with ground-glass stoppers or foil-liner screw caps.

5.3 Lauric acid - reagent grade. Used for the standardization of the Florisil activity. Weigh 10.00 g of lauric acid in a 500-mL volumetric flask. Add 50 mL of hexane to the flask to dissolve the lauric acid. Swirl the flask gently until the lauric acid is dissolved, then dilute the solution in the flask to 500 mL with additional hexane.

5.4 Phenolphthalein Indicator - Dissolve 1 g of phenolphthalein in ethanol and dilute to 100 mL in a 100-mL volumetric flask.

5.5 Sodium hydroxide - Weigh out 20 g of NaOH (pellets, reagent grade) in a 500-mL volumetric flask. Dissolve in organic-free reagent water and dilute to 500 mL to make a 1 N solution. Dilute 25 mL of the 1 N NaOH to 500 mL with water in a second 500-mL volumetric flask, yielding a 0.05N solution. The NaOH solution must be standardized against lauric acid, as follows.

5.5.1 Weigh 100 - 200 mg of lauric acid to the nearest 1 mg in a 125-mL Erlenmeyer flask. Add 50 mL of ethanol to the flask and swirl to dissolve the lauric acid.

5.5.2 Add 3 drops of phenolphthalein indicator to the flask, and titrate with the 0.05 N NaOH solution to a permanent endpoint (i.e., the indicator color does not disappear when the solution is allowed to stand for 1 min).

5.5.3 Calculate the "strength" of the NaOH solution as the mg of lauric acid neutralized per mL of NaOH solution.

5.6 Deactivation/Activation of Florisil

5.6.1 Deactivation of Florisil - for cleanup of phthalate esters. To prepare for use, place 100 ± 10 g of Florisil into a 500-mL beaker and heat to 140°C for approximately 16 h. After heating, transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool, add 3 ± 0.1 mL of organic-free reagent water. Mix thoroughly by shaking or rolling for 10 min and let stand for at least 2 h. Keep the bottle sealed tightly.

5.6.2 Activation of Florisil - for all cleanups other than phthalate esters. It is advisable to treat both Florisil A and Florisil PR prior to use to drive off any moisture adsorbed during storage and handling. Heat the Florisil in a glass container loosely covered with aluminum foil in an oven at 130°C overnight. Cool the Florisil in a dessicator before use.

5.6.3 Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, use the lauric acid value, described below. The procedure determines the adsorption from a hexane solution of lauric acid (mg) per g of Florisil.

5.6.3.1 Weigh 2.000 g of Florisil in a 25-mL glass-stoppered Erlenmeyer flask. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper the flask and cool to room temperature.

5.6.3.2 Add 20.0 mL of the lauric acid solution to the flask, stopper, and shake occasionally for 15 min.

5.6.3.3 Let the Florisil settle and using a volumetric pipet, transfer 10.0 mL of supernatant liquid into a 125-mL Erlenmeyer flask. Avoid inclusion of any Florisil.

5.6.3.4 Add 60 mL of ethanol and 3 drops of the phenolphthalein indicator solution to the flask.

5.6.3.5 Titrate the solution in the flask with the 0.05N NaOH solution until a permanent end point is reached (i.e., the indicator color does not disappear when the solution is allowed to stand for 1 min).

5.6.3.6 The lauric acid value is calculated as follows:

$$\text{Lauric acid value} = 200 - (\text{titration volume in mL of NaOH})\,(\text{strength of NaOH})$$

where the strength of the NaOH is measured in Sec. 7.5.3 as the mg of lauric acid neutralized per mL of NaOH solution.

5.6.3.7 Use the following equation to obtain an equivalent quantity of any batch of Florisil.

$$\frac{\text{lauric acid value}}{110} \times 20\ \text{g} = \text{Required weight of Florisil}$$

5.7 Sodium sulfate (granular, anhydrous), Na_2SO_4 - Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. A method blank must be analyzed in order to demonstrate that there is no interference from the sodium sulfate.

5.8 Florisil cartridges - 40 µm particles, 60 Å pores. The cartridges from which this method were developed consist of 6-mL serological- grade polypropylene tubes, with the 1 g of Florisil held between two polyethylene or stainless steel frits with 20 µm pores. Cartridges containing 0.5 g and 2.0 g of Florisil are available, however, the compound elution patterns must be verified when cartridges containing other than 1 g of Florisil are used.

5.9 Eluting solvents - all solvents must be pesticide quality or equivalent.

5.9.1 Diethyl Ether, $C_2H_5OC_2H_5$. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.9.2 Pentane, $CH_3(CH_2)_3CH_3$

5.9.3 Hexane, C_6H_{14}

5.9.4 Methylene chloride, CH_2Cl_2

5.9.5 Acetone, CH_3COCH_3

5.9.6 Petroleum ether (boiling range 30-60°C)

5.9.7 Toluene, $C_6H_5CH_3$

5.9.8 2-Propanol, $(CH_3)_2CHOH$

5.10 Florisil cartridge phenol check solution (for the organochlorine pesticide technique) - Prepare a solution of 2,4,5-Trichlorophenol in acetone at a concentration of 0.1 mg/L.

5.11 Florisil cartridge pesticide check solution - Prepare a solution containing the following analytes in hexane:

α-BHC	5 mg/L
Heptachlor	5 mg/L
γ-BHC	5 mg/L
Endosulfan I	5 mg/L
Dieldrin	10 mg/L
Endrin	10 mg/L
4,4'-DDD	10 mg/L
4,4'-DDT	10 mg/L
Methoxychlor	50 mg/L
Tetrachloro-m-xylene	20 mg/L
Decachlorobiphenyl	20 mg/L

5.12 Chlorophenoxy acid herbicide check solution - Prepare a solution containing 2,4,5-T methyl ester at 100 mg/L, pentachlorophenyl methyl ester at 50 mg/L, and Picloram methyl ester at 200 mg/L.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

Sec. 7.1 describes the procedures for assembling and conditioning the Florisil cartridges. Sec. 7.2 describes general procedures for handling sample extracts prior to cleanup. Secs. 7.3 - 7.13 describe the column and cartridge procedures for phthalate esters; nitrosamines; organochlorine pesticides, haloethers, and organophosphorus pesticides; nitroaromatics and isophorone; chlorinated hydrocarbons; aniline and aniline derivatives; organophosphates; and derivatized chlorophenoxy acid herbicides.

The column chromatography procedures employ a larger amount of Florisil than the cartridge procedures and, therefore, have a greater cleanup capacity. Samples that exhibit greater degrees of interferences should be cleaned up using the column procedures. However, both techniques have limitations on the amount of interferences that they can remove.

If the interference is caused by high boiling materials, then Method 3640 should be employed prior to Florisil cleanup. If the interference is caused by relatively polar compounds in the same boiling range as the analytes of interest, then multiple column or cartridge cleanups may be required. For additional cleanup of organochlorine pesticides and PCBs, see Method 3665. If crystals of sulfur are present in the extract, then Method 3660 should be employed prior to Florisil cleanup.

Whenever Florisil is used to fractionate groups of target compounds (rather than to simply remove potential interferents) it is critical that the specific fractionation scheme be validated using

spiked solutions or spiked sample extracts that contain most or all of the analytes of interest. This may be particularly important when the Florisil cartridge techniques are employed, as the differences between the various cartridge formats and manufacturers may affect the fractionation patterns. In addition, it may be useful to archive any fractions not originally intended for analysis, in the event that the fractionation scheme chosen does not yield the intended results. Once the determinative analysis has been performed and demonstrates that the fractionation has been successful, such archived fractions may be disposed of in an appropriate manner. However, if the fractionation did not perform as intended, the analytes of interest may be contained in the archived fractions which may be able to be analyzed or combined with the other fraction(s) for reanalysis.

Following Florisil cleanup, extracts may require further concentration and/or solvent exchange. Consult the appropriate determinative method and 3500 Series extraction method for details.

7.1 Cartridge set-up and conditioning

7.1.1 Arrange the cartridges on the manifold in the closed-valve position.

7.1.2 Turn on the vacuum pump and set the vacuum to 10 in (254 mm) of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates may be controlled by opening and closing cartridge valves.

7.1.3 Condition the cartridges by adding 4 mL of hexane to each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes. Do not turn off the vacuum.

7.1.4 Slowly open cartridge valves to allow the hexane to pass through the cartridges. Close the cartridge valves when there is still at least 1 mm of solvent above the sorbent bed. Do not allow cartridges to become dry. If cartridges go dry, repeat the conditioning step.

7.2 Handling sample extracts

Most sample extracts will have to be concentrated to a smaller volume prior to the use of Florisil cleanup. The extract volume is a function of the analytical sensitivity necessary to meet the project objectives. The extract volume will also affect the ability of the Florisil to separate target analytes from potential interferences, particularly for the cartridge procedures, where applying large extract volumes to the cartridges may cause poor results. As noted in Sec. 7.0, consult the appropriate extraction and determinative methods for the details on final extract volumes, extract concentration techniques, and solvent exchange procedures.

7.2.1 Reduce the sample extract volume to 2 mL prior to cleanup for:

Phthalate esters	Chlorinated hydrocarbons
Nitrosamines	Chlorophenoxy acid herbicides
Nitroaromatics and isophorone	Aniline and aniline derivatives

The extract solvent should be hexane for the phthalate esters, nitroaromatics, chlorinated hydrocarbons, and chlorophenoxy acid herbicides, and methylene chloride for the nitrosamines and aniline and aniline derivatives.

7.2.2 Reduce the sample extract volume to 10 mL prior to cleanup for:

Organochlorine pesticides
Haloethers
Organophosphorus pesticides
Organophosphates
PCBs

The extract solvent should be hexane for these analytes. In most cases, given the sensitivity of the determinative methods, only 1 mL of the 10 mL extract needs to be subjected to the Florisil cleanup procedure. The remaining 9 mL should be archived for later use, if needed.

7.2.3 Allow the extract to reach room temperature if it was in cold storage. Inspect the extract visually to ensure that there are no particulates or phase separations and that no evaporative loss has taken place. If crystals of sulfur are visible or if the presence of sulfur is suspected, proceed with Method 3660.

7.3 Column procedure for phthalate esters

7.3.1 Place approximately 10 g of deactivated Florisil (Sec. 5.2.1) into a 10 mm ID chromatographic column. Tap the column to settle the Florisil and add approximately 1 cm of anhydrous sodium sulfate to the top.

7.3.2 Pre-elute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer.

7.3.3 Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.3.4 Elute the column with 100 mL of ethyl ether/hexane (20/80, v/v) and collect this fraction in a flask (e.g., a 500 mL K-D flask equipped with a clean 10 mL concentrator tube). Concentrate the eluate to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method. No solvent exchange is necessary. Compounds that elute in this fraction are:

Bis(2-ethylhexyl) phthalate	Diethyl phthalate
Butyl benzyl phthalate	Dimethyl phthalate
Di-n-butyl phthalate	Di-n-octyl phthalate

7.4 Cartridge procedure for phthalate esters

7.4.1 Using 1-g Florisil cartridges, condition the cartridges with hexane as described in Sec. 7.1.

7.4.2 Transfer the extract (Sec. 7.2) to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.4.3 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vials with an additional 0.5 mL of solvent, and add the rinse to the cartridges to complete the quantitative transfer.

7.4.4 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never gets dry.

7.4.5 Place a 5-mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align it with the collection vial.

7.4.6 If the sample is suspected to contain organochlorine pesticides, elute the cartridge with methylene chloride/hexane (20/80, v/v). Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve, and collect the eluate (this fraction contains the organochlorine pesticides, and should be discarded).

7.4.7 Close the cartridge valve, replace collection vials, and add 10 mL of acetone/hexane (10/90, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This fraction contains the phthalate esters, and should be retained for analysis.

7.4.8 Concentrate the eluate to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.5 Column procedure for nitrosamines

7.5.1 Add a weight of activated Florisil (nominally 22 g) predetermined by calibration (Sec. 5.6.3.7) into a 20 mm ID chromatographic column. Tap the column to settle the Florisil and add about 5 mm of anhydrous sodium sulfate to the top.

7.5.2 Pre-elute the column with 40 mL of ethyl ether/pentane (15/85, v/v). Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract (Sec. 7.2) onto the column using an additional 2 mL of pentane to complete the transfer.

7.5.3 Just prior to the exposure of the sodium sulfate layer to the air, elute the column with 90 mL of ethyl ether/pentane (15/85, v/v). Discard the eluate. This fraction will contain and diphenylamine present in the extract.

7.5.4 Elute the column with 100 mL of acetone/ethyl ether (5/95, v/v), collecting the eluate in a flask (e.g., a 500 mL K-D flask equipped with a clean 10 mL concentrator tube). This fraction will contain all of the nitrosamines listed in the scope of the method.

7.5.5 Add 15 mL of methanol to the collected fraction, and concentrate this fraction to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.6 Column procedure for organochlorine pesticides, haloethers, and organophosphorus pesticides (see Table 2 for fractionation patterns of organophosphorus pesticides)

7.6.1 Add a weight of activated Florisil (nominally 20 g), predetermined by calibration (Sec. 5.6.3.7), to a 20 mm ID chromatographic column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep.

7.6.2 Pre-elute the column with 60 mL of hexane and discard the eluate. Just prior to exposure of the sodium sulfate to air, quantitatively transfer the 10-mL sample extract (Sec. 7.2) onto the column, completing the transfer with two 1-2 mL rinses with hexane.

7.6.3 Place a flask (e.g., a 500 mL K-D flask equipped with a clean concentrator tube) under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of ethyl ether/hexane (6/94, v/v) using a drip rate of about 5 mL/min. This is Fraction 1, and all of the haloethers are in this fraction. Remove the flask and set aside for later concentration.

7.6.4 Elute the column again, using 200 mL of ethyl ether/hexane (15/85, v/v), into a second flask. This is Fraction 2.

7.6.5 Perform a third elution using 200 mL of diethyl ether/hexane (50/50, v/v), collecting the eluate in a third flask. This is Fraction 3.

7.6.6 Perform a final elution with 200 mL of 100% ethyl ether, collecting the eluate in a fourth flask. This is Fraction 4.

7.6.7 Concentrate the four eluates to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.7 Cartridge procedure for organochlorine pesticides and PCBs

7.7.1 Using 1-g Florisil cartridges, condition the cartridges with hexane, as described in Sec. 7.1.

7.7.2 Transfer the 1 mL (or other appropriate volume) of the extract (Sec. 7.2) to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.7.3 When the entire extract has passed through the cartridge, but before the cartridge becomes dry, rinse the sample vial with an additional 0.5 mL of hexane, and add the rinse to the cartridge to complete the quantitative transfer.

7.7.4 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never goes dry.

7.7.5 Place a 10-mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align with the collection vial.

7.7.6 If there is no need to separate the organochlorine pesticides from the PCBs, then add 9 mL of acetone/hexane (10/90, v/v) to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial. Go directly to Sec. 7.7.8.

7.7.7 The following procedures are used to separate the organochlorine pesticides from the PCBs.

7.7.7.1 Add 3 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 1 and it will contain the PCBs and a few of the organochlorine pesticides (see Table 5).

7.7.7.2 Close the cartridge valve, replace the collection vial, and add 5 mL of methylene chloride/hexane (26/74, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 2 and it will contain most of the pesticides.

7.7.7.3 Close the cartridge valve, replace collection vials, and add 5 mL of acetone/hexane (10/90, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 3 and it will contain the remaining pesticides.

7.7.8 As needed, perform a solvent exchange and adjust the final volume of the eluant to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.8 Column procedure for nitroaromatics and isophorone

7.8.1 Add a weight of activated Florisil (nominally 10 g) predetermined by calibration (Sec. 5.6.3.7) into a 10 mm ID chromatographic column. Tap the column to settle the Florisil and add about 1 cm of anhydrous sodium sulfate to the top.

7.8.2 Pre-elute the column with methylene chloride/hexane (10/90, v/v) at about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract (Sec. 7.2) onto the column using an additional 2 mL of hexane to complete the transfer.

7.8.3 Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of methylene chloride/hexane (10/90, v/v) and continue the elution of the column. Discard the eluate.

7.8.4 Elute the column with 90 mL of ethyl ether/pentane (15/85, v/v) and discard the eluate. This fraction will contain any diphenylamine present in the extract.

7.8.5 Elute the column with 100 mL of acetone/ethyl ether (5/95, v/v), and collect the eluate in a flask (e.g., a 500 mL K-D flask equipped with a 10-mL concentrator tube). This fraction will contain all of the nitrosamines listed in the scope of the method.

7.8.6 Add 15 mL of methanol to the collected fraction, and concentrate to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.8.7 Elute the column with 30 mL of acetone/methylene chloride (10/90, v/v), and collect the eluate in a flask (e.g., a 500-mL K-D flask equipped with a 10-mL concentrator tube). Concentrate the collected fraction to the volume listed in the determinative method,

using the techniques described in the appropriate 3500 series method, and exchanging the solvent to hexane. Compounds that elute in this fraction are:

2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Nitrobenzene

7.9 Column procedure for chlorinated hydrocarbons

7.9.1 Add a weight of activated Florisil (nominally 12 g) predetermined by calibration (Sec. 5.6.3.7) into a 10 mm ID chromatographic column. Tap the column to settle the Florisil and add about 1 to 2 cm of anhydrous sodium sulfate to the top.

7.9.2 Pre-elute the column with 100 mL of petroleum ether. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract (Sec. 7.2) to the column by decantation and subsequent petroleum ether washings. Discard the eluate.

7.9.3 Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL of petroleum ether and collect the eluate in flask (e.g., a 500-mL K-D flask equipped with a 10-mL concentrator tube).

This fraction should contain the following chlorinated hydrocarbons:

2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2,4-Trichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane

7.9.4 Concentrate the collected fraction to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.10 Cartridge procedure for chlorinated hydrocarbons

7.10.1 Using 1-g Florisil cartridges, condition the cartridges with 5 mL of acetone/hexane (10/90, v/v) as described in Sec. 7.1.

7.10.2 Transfer the extract (Sec. 7.2) to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.10.3 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vial with an additional 0.5 mL of acetone/hexane (10/90), and add the rinse to the cartridges to complete the quantitative transfer.

7.10.4 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never gets dry.

7.10.5 Place a 5-mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align it with the collection vial.

7.10.6 Add 10 mL of acetone/hexane (10/90, v/v) to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial.

7.10.7 Adjust the final volume of the eluant to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.11 Column procedure for Aniline and Aniline derivatives (see Table 4 for elution patterns)

7.11.1 Add a weight of activated Florisil predetermined by calibration (Sec. 5.6.3.7) into a 20 mm ID chromatographic column. Tap the column to settle the Florisil.

7.11.2 Pre-elute the column with 100 mL of 2-propanol/methylene chloride (5/95, v/v), followed by 100 mL of hexane/methylene chloride (50/50, v/v), followed by 100 mL of hexane. Discard the eluate and leave a column of about 5 cm of hexane above the Florisil.

7.11.3 Quantitatively transfer the 2-mL sample extract (Sec. 7.2) onto 2.0 g of activated Florisil in a 50-mL beaker, using a small volume of methylene chloride, and dry under a gentle stream of nitrogen.

7.11.4 Place the dried Florisil containing the sample extract onto the chromatographic column, and wash the beaker which contained the Florisil with 75 mL of hexane, adding this wash to the reservoir.

7.11.5 Elute the hexane from the column and discard. Stop the column flow just prior to the exposure of the Florisil to air.

7.11.6 Elute the column with 50 mL of methylene chloride/hexane (50/50, v/v), using a drip rate of about 5 mL/minute, and collect the eluate in a flask (e.g., a 500-mL K-D flask equipped with a 10-mL concentrator tube). This is Fraction 1.

7.11.7 Elute the column with 50 mL of 2-propanol/hexane (5/95, v/v), and collect the eluate in a second flask. This is Fraction 2.

7.11.8 Elute the column a third time using 50 mL of methanol/hexane (5/95, v/v). Collect the eluate in a third flask. This is Fraction 3. Frequently, it will prove useful to combine the three fractions prior to analysis. However, in some situations, analysis of each separate fraction may be required. Refer to Method 8131.

7.11.9 Concentrate the collected fractions to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.12 Column procedure for organophosphates

7.12.1 Add a weight of activated Florisil, predetermined by calibration (Sec. 5.6.3.7), to a 20 mm ID chromatographic column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep.

7.12.2 Pre-elute the column with 50-60 mL of hexane. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the 10-mL sample extract (Sec. 7.2) onto the column using a hexane wash to complete the transfer.

7.12.3 Just as the sample reaches the sodium sulfate, elute the column with 100 mL of diethyl ether/hexane (10/90, v/v). Discard the eluate.

7.12.4 Just prior to exposure of the sodium sulfate to air, elute the column with 200 mL of diethyl ether/hexane (30/70, v/v). This fraction contains all of the target analytes except for tris(2,3-dibromopropyl) phosphate.

7.12.5 Elute the column with 200 mL of diethyl ether/hexane (40/60, v/v). This fraction contains tris(2,3-dibromopropyl) phosphate.

7.12.6 Concentrate the collected fraction to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

7.13 Column procedure for derivatized chlorophenoxy acid herbicides

7.13.1 Add a weight of activated Florisil (nominally 4 g) predetermined by calibration (Sec. 5.6.3.7) into a 20 mm ID chromatographic column. Tap the column to settle the Florisil and add approximately 5 mm of anhydrous sodium sulfate to the top.

7.13.2 Pre-elute the column with 15 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate, and just prior to exposure of the sodium sulfate to air, quantitatively transfer the 2-mL sample extract (Sec. 7.2) onto the column, using an additional 2 mL of hexane to complete the transfer.

7.13.3 Just prior to the exposure of the sodium sulfate layer to the air, elute the column with 35 mL of methylene chloride/hexane (20/80, v/v), collecting the eluate in a clean flask (e.g., a 500 mL K-D flask equipped with a concentrator tube). This is Fraction 1, and will contain any pentachlorophenyl methyl ester that is present.

7.13.4 Elute the column with 60 mL of methylene chloride/acetonitrile/hexane (50/0.035/49.65, v/v/v), collecting the eluate in a second flask. This is Fraction 2.

7.13.5 If Picloram is to be determined, perform a third elution with the volume of diethyl ether determined from the Florisil check in Sec. 8.2.4, collecting this eluate in a third flask. This is Fraction 3, and will contain the Picloram.

7.13.6 The three fractions may be combined for analysis. Concentrate the combined fractions to the volume listed in the determinative method, using the techniques described in the appropriate 3500 series method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples. This test applies to both the column cleanup and cartridge cleanup procedures. A recovery check must be performed using standards of the target analytes at known concentration.

8.2.1 This test must be conducted on each batch of Florisil following its activation (Sec. 5.4).

8.2.2 The efficiency of each lot of the solid-phase extraction cartridges must be verified. Only lots of cartridges from which the spiked analytes are quantitatively recovered may be used to process the samples. A check should also be performed at least once on each individual lot of cartridges and at least once for every 300 cartridges of a particular lot, whichever frequency is greater.

8.2.3 Organochlorine pesticides - To check each new lot of Florisil cartridges before use, perform the following in duplicate:

8.2.3.1 Combine 0.5 mL of the 2,4,5-trichlorophenol solution in Sec. 5.10, 1.0 mL of the pesticide solution in Sec. 5.11, and 0.5 mL of hexane in a vial.

8.2.3.2 Condition the cartridge as described in Sec. 7.1 and then perform the cartridge cleanup starting with Sec. 7.7.

8.2.3.3 Elute the cartridge with 9 mL of acetone/hexane (10/90, v/v) only. Reduce the volume to 1.0 mL and analyze by Method 8081.

8.2.3.4 The lot of Florisil cartridges is acceptable if all pesticides are recovered at 80 to 110 %, if the recovery of trichlorophenol is less than 5 %, and if no peaks interfering with the target analytes are detected.

8.2.4 Chlorophenoxy acid herbicides - To check each new lot of granular Florisil perform the following:

8.2.4.1 Add 5 mL of the chlorophenoxy acid herbicide check solution (Sec. 5.12) to a Florisil column packed and washed as in Sec. 7.13.2.

8.2.4.2 Elute Fractions 1 and 2 as described in Secs. 7.13.3 and 7.13.4, collecting each in a separate flask.

8.2.4.3 Elute the column with approximately 100 mL diethyl ether and collect ten separate 10-mL fractions.

8.2.4.4 Concentrate Fraction 1 and Fraction separately and concentration each of the ten 10-mL diethyl ether fractions to 5 mL.

8.2.4.5 Analyze each of the 12 eluates by GC/ECD and calculate the recovery of each analyte. Pentachlorophenyl methyl ether should be found in Fraction 1. 2,4,5-T methyl ester (and the methyl esters of the other chlorophenoxy acids) should be found in Fraction 2. Determine the volume of diethyl ether that is required to elute Picloram methyl ester.

8.2.4.6 The lot of Florisil is acceptable if the target analytes are quantitatively recovered and if the recovery of trichlorophenol is less than 5%. No interferences should be detected in any of these eluates.

8.3 The quality control samples associated with sample extracts that are cleaned up using this method must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides recoveries of phthalate esters obtained from the Florisil column procedure.

9.2 Table 2 provides recoveries of phthalate esters obtained from the Florisil cartridge procedure.

9.3 Table 3 provides the distribution of organochlorine pesticides and PCBs from the Florisil column procedure.

9.4 Table 4 provides recoveries of Aroclors from the Florisil cartridge procedure.

9.5 Table 5 provides the distribution of organochlorine pesticides from the Florisil cartridge procedure, using 1-g cartridges.

9.6 Table 6 provides the distribution of organophosphorus pesticides from the Florisil column procedure.

9.7 Table 7 provides recoveries of chlorinated hydrocarbons obtained from the Florisil cartridge procedure.

9.8 Table 8 provides the elution patterns for aniline compounds from the Florisil column procedure.

10.0 REFERENCES

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7. US EPA Method 650, Aniline and Selected Substituted Derivatives.

8. Beckert, W.F., and Lopez-Avila, V., "Evaluation of SW-46 Method 8060 for Phthalate Esters," Proceedings of the Fifth Annual Waste Testing and Quality Assurance Symposium, 1989, pp. 144-156.

9. US EPA Method 608, Organochlorine Pesticides and PCBs.

TABLE 1

AVERAGE RECOVERIES OF 16 PHTHALATE ESTERS FROM THE FLORISIL COLUMN PROCEDURE[a]

Compound	Average % Recovery
Dimethyl phthalate	40
Diethyl phthalate	57
Diisobutyl phthalate	80
Di-n-butyl phthalate	85
Bis(4-methyl-2-pentyl) phthalate	84
Bis(2-methoxyethyl) phthalate	0
Diamyl phthalate	82
Bis(2-ethoxyethyl) phthalate	0
Hexyl 2-ethylhexyl phthalate	105
Dihexyl phthalate	74
Benzyl butyl phthalate	90
Bis(2-n-butoxyethyl) phthalate	0
Bis(2-ethylhexyl) phthalate	82
Dicyclohexyl phthalate	84
Di-n-octyl phthalate	115
Dinonyl phthalate	72

[a] Average recovery from two determinations, data from Reference 8.

TABLE 2

AVERAGE RECOVERIES OF 16 PHTHALATE ESTERS FROM FLORISIL CARTRIDGES[a]

Compound	Average % Recovery
Dimethyl phthalate	89
Diethyl phthalate	97
Diisobutyl phthalate	92
Di-n-butyl phthalate	102
Bis(4-methyl-2-pentyl) phthalate	105
Bis(2-methoxyethyl) phthalate	78
Diamyl phthalate	94
Bis(2-ethoxyethyl) phthalate	94
Hexyl 2-ethylhexyl phthalate	96
Dihexyl phthalate	97
Benzyl butyl phthalate	99
Bis(2-n-butoxyethyl) phthalate	92
Bis(2-ethylhexyl) phthalate	98
Dicyclohexyl phthalate	90
Di-n-octyl phthalate	97
Dinonyl phthalate	105

[a] Average recovery from two determinations, data from Reference 6.

TABLE 3

DISTRIBUTION OF ORGANOCHLORINE PESTICIDES AND PCBs
IN FLORISIL COLUMN FRACTIONS

Compound	Percent Recovery by Fraction[a] 1	2	3
Aldrin	100		
α-BHC	100		
β-BHC	97		
δ-BHC	98		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
Aroclor 1016	97		
Aroclor 1221	97		
Aroclor 1232	95	4	
Aroclor 1242	97		
Aroclor 1248	103		
Aroclor 1254	90		
Aroclor 1260	95		

[a] Eluant composition:
Fraction 1 - 200 mL of 6% ethyl ether in hexane
Fraction 2 - 200 mL of 15% ethyl ether in hexane
Fraction 3 - 200 mL of 50% ethyl ether in hexane

Data from Reference 9.

TABLE 4

AVERAGE RECOVERIES OF AROCLORS FROM FLORISIL CARTRIDGES

Compound	Average % Recovery
Aroclor 1016	105
Aroclor 1221	76
Aroclor 1232	90
Aroclor 1242	94
Aroclor 1248	97
Aroclor 1254	95
Aroclor 1260	90

TABLE 5

ELUTION PATTERNS AND RECOVERIES OF ORGANOCHLORINE PESTICIDES FROM FLORISIL CARTRIDGES[a]

Compound	Fraction 1		Fraction 2		Fraction 3	
	Rec.	RSD	Rec.	RSD	Rec.	RSD
α-BHC	-	-	111	8.3	-	-
β-BHC	-	-	109	7.8	-	-
γ-BHC	-	-	110	8.5	-	-
δ-BHC	-	-	106	9.3	-	-
Heptachlor	98	11	-	-	-	-
Aldrin	97	10	-	-	-	-
Heptachlor epoxide	-	-	109	7.9	-	-
Chlordane	-	-	105	3.5	-	-
Endosulfan I	-	-	111	6.2	-	-
4,4'-DDE	104	5.7	-	-	-	-
Dieldrin	-	-	110	7.8	-	-
4,4'-DDD	-	-	111	6.2	-	-
Endosulfan II	-	-	-	-	111	2.3
Endrin aldehyde	-	-	49	14	48	12
4,4'-DDT[b]	40	2.6	17	24	63	3.2
Endosulfan sulfate[b]	-	-	-	-	-	-
Methoxychlor	-	-	85	2.2	37	29

[a]1-g Florisil cartridges spiked with 0.5 µg of each compound.

[b]These two compounds coelute on the DB-5 capillary column.

Eluant composition:
Fraction 1 - 3 mL of hexane
Fraction 2 - 5 mL of methylene chloride/hexane (26/74, v/v)
Fraction 3 - 5 mL of acetone/hexane (10/90, v/v)

TABLE 6

DISTRIBUTION OF ORGANOPHOSPHORUS PESTICIDES
IN FLORISIL CLEANUP FRACTIONS

Compound	Percent Recovery by Fraction[a] 1	2	3	4
Azinphos methyl			20	80
Bolstar (Sulprofos)	ND	ND	ND	ND
Chlorpyrifos	>80			
Coumaphos	NR	NR	NR	
Demeton	100			
Diazinon		100		
Dichlorvos	NR	NR	NR	
Dimethoate	ND	ND	ND	ND
Disulfoton	25-40			
EPN		>80		
Ethoprop	V	V	V	
Fensulfothion	ND	ND	ND	ND
Fenthion	R	R		
Malathion		5	95	
Merphos	V	V	V	
Mevinphos	ND	ND	ND	ND
Monochrotophos	ND	ND	ND	ND
Naled	NR	NR	NR	
Parathion		100		
Parathion methyl		100		
Phorate	0-62			
Ronnel	>80			
Stirophos (Tetrachlorvinphos)	ND	ND	ND	ND
Sulfotepp	V	V		
TEPP	ND	ND	ND	ND
Tokuthion (Prothiofos)	>80			
Trichloronate	>80			

[a]Eluant composition:
Fraction 1 - 200 mL of 6% ethyl ether in hexane
Fraction 2 - 200 mL of 15% ethyl ether in hexane
Fraction 3 - 200 mL of 50% ethyl ether in hexane
Fraction 4 - 200 mL of 100% ethyl ether

R = Recovered (no percent recovery data provided by U.S. FDA)
NR = Not recovered (U. S. FDA)
V = Variable recovery (U. S. FDA)
ND = Not determined

TABLE 7

PERCENT RECOVERIES AND ELUTION PATTERNS FOR 22 CHLORINATED HYDROCARBONS FROM 1-g FLORISIL CARTRIDGES[a]

Compound	Fraction 2 Average % Recovery	Fraction 2 Average RSD
Hexachloroethane	95	2.0
1,3-Dichlorobenzene	101	2.3
1,4-Dichlorobenzene	100	2.3
1,2-Dichlorobenzene	102	1.6
Benzyl chloride	101	1.5
1,3,5-Trichlorobenzene	98	2.2
Hexachlorobutadiene	95	2.0
Benzal chloride	99	0.8
1,2,4-Trichlorobenzene	99	0.8
Benzotrichloride	90	6.5
1,2,3-Trichlorobenzene	97	2.0
Hexachlorocyclopentadiene	103	3.3
1,2,4,5-Tetrachlorobenzene	98	2.3
1,2,3,5-Tetrachlorobenzene	98	2.3
1,2,3,4-Tetrachlorobenzene	99	1.3
2-Chloronaphthalene	95	1.4
Pentachlorobenzene	104	1.5
Hexachlorobenzene	78	1.1
alpha-BHC	100	0.4
gamma-BHC	99	0.7
beta-BHC	95	1.8
delta-BHC	97	2.7

[a]Florisil cartridges (Supelco, Inc.) were conditioned with 4 mL of hexane. Five replicate experiments were performed. The cartridges were spiked with 1.0 µg per cartridge for hexachloroethane, hexachlorobutadiene, hexachloropentadiene, pentachlorobenzne, and hexachlorobenzene. The trichlorobenzenes, tetrachlorobenzenes, benzal chloride, benzotrichloride, and the BHCs were spiked at 10 µg per cartridge. The dichlorobenzenes and benzyl chloride were spiked at 100 µg per cartridge, and 2-chloronaphthalene was spiked at 200 µg per cartridge. The cartridges were eluted with 5 mL of acetone/hexane (10/90, v/v).

TABLE 8

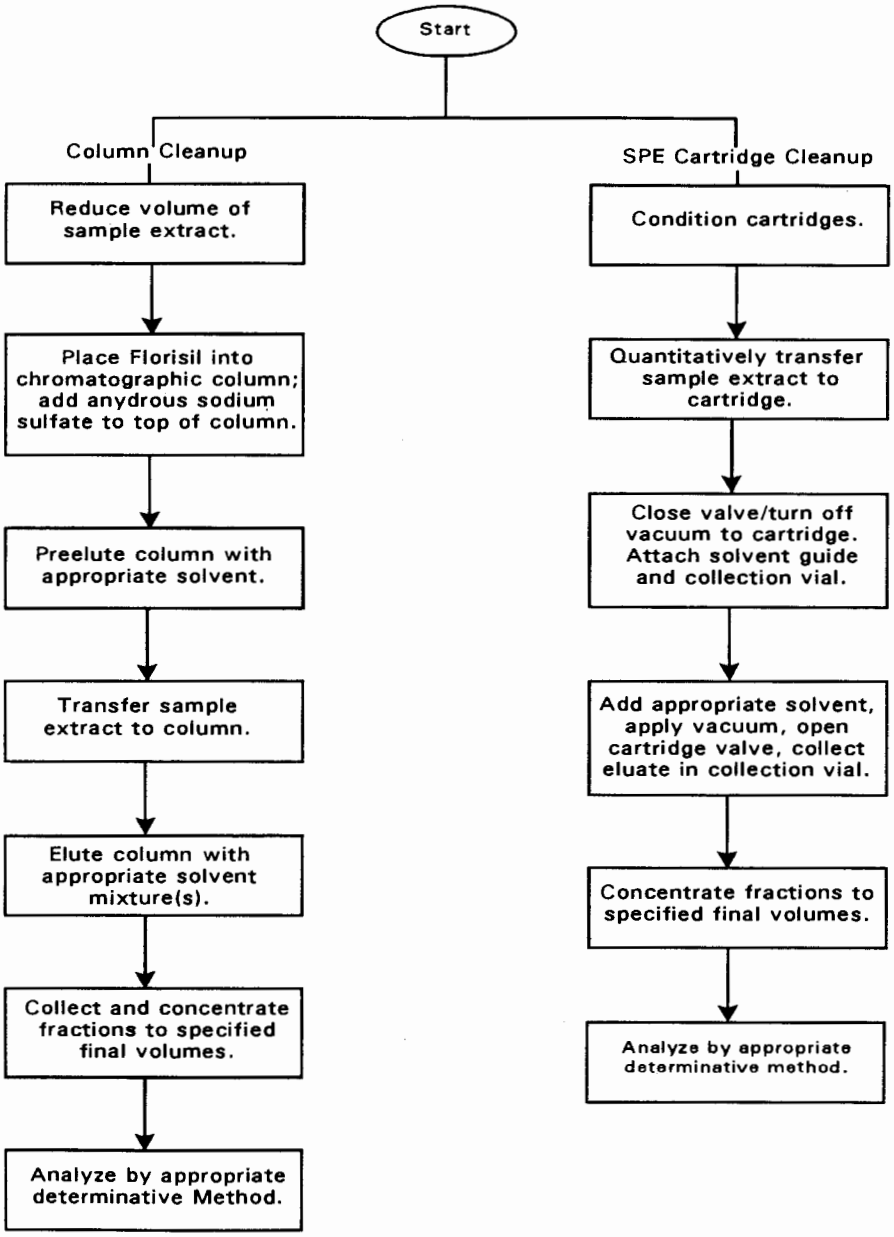
DISTRIBUTION OF ANILINES IN FLORISIL CLEANUP FRACTIONS

Compound	Percent Recovery by Fraction 1	2	3
Aniline		41	52
2-Chloroaniline		71	10
3-Chloroaniline		78	4
4-Chloroaniline	7	56	13
4-Bromoaniline		71	10
3,4-Dichloroaniline		83	1
2,4,6-Trichloroaniline	70	14	
2,4,5-Trichloroaniline	35	53	
2-Nitroaniline		91	9
3-Nitroaniline		89	11
4-Nitroaniline		67	30
2,4-Dinitroaniline			75
4-Chloro-2-nitroaniline		84	
2-Chloro-4-nitroaniline		71	10
2,6-Dichloro-4-nitroaniline		89	9
2,6-Dibromo-4-nitroaniline		89	9
2-Bromo-6-chloro-4-nitroaniline		88	16
2-Chloro-4,6-dinitroaniline			76
2-Bromo-4,6-dinitroaniline			100

Eluant composition:

Fraction 1 - 50% methylene chloride in hexane
Fraction 2 - 5% 2-propanol in hexane
Fraction 3 - 5% methanol in hexane

METHOD 3620B
FLORISIL CLEANUP



Note: Select specific procedures provided in the method depending on the type(s) of analytes of interest. See the method for details regarding the appropriate elution and collection procedures.

METHOD 3630C

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel (silicic acid) is a regenerative adsorbent of silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used in column chromatography for the separation of analytes from interfering compounds of a different chemical polarity. It may be used activated, after heating to 150 - 160°C, or deactivated with up to 10% water.

1.2 This method includes guidance for standard column cleanup of sample extracts containing polynuclear aromatic hydrocarbons, derivatized phenolic compounds, organochlorine pesticides, and PCBs as Aroclors.

1.3 This method also provides cleanup procedures using solid-phase extraction cartridges for pentafluorobenzyl bromide-derivatized phenols, organochlorine pesticides, and PCBs. This technique also provides the best separation of PCBs from most single component organochlorine pesticides. When only PCBs are to be measured, this method can be used in conjunction with sulfuric acid/permanganate cleanup (Method 3665).

1.4 Other analytes may be cleaned up using this method if the analyte recovery meets the criteria specified in Sec. 8.0.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides the option of using either standard column chromatography techniques or solid-phase extraction cartridges. Generally, the standard column chromatography techniques use larger amounts of adsorbent and, therefore, have a greater cleanup capacity.

2.2 In the standard column cleanup protocol, the column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is accomplished with a suitable solvent(s) that leaves the interfering compounds on the column. The eluate is then concentrated (if necessary).

2.3 The cartridge cleanup protocol uses solid-phase extraction cartridges packed with 1 g or 2 g of silica gel (silicic acid) adsorbent. Each cartridge is solvent washed immediately prior to use. Aliquots of sample extracts are loaded onto the cartridges, which are then eluted with suitable solvent(s). A vacuum manifold is required to obtain reproducible results. The collected fractions may be further concentrated prior to gas chromatographic analysis.

2.4 The appropriate gas chromatographic method is listed at the end of each technique. Analysis may also be performed by gas chromatography/mass spectrometry (Method 8270).

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks. See Sec. 8 for guidance on a reagent blank check.

3.2 Phthalate ester contamination may be a problem with certain cartridges The more inert the column and/or cartridge material (i.e., glass or polytetrafluoroethylene (PTFE)), the less problem with phthalates. Phthalates create interference problems for all method analytes, not just the phthalate esters themselves.

3.3 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column - 250 mm long x 10 mm ID; with Pyrex® glass wool at bottom and a PTFE stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers - appropriate sizes.

4.3 Vials - 2, 10, 25 mL, glass with PTFE-lined screw-caps or crimp tops.

4.4 Muffle furnace.

4.5 Reagent bottle - appropriate sizes.

4.6 Erlenmeyer flasks - 50 and 250 mL.

4.7 Vacuum manifold: VacElute Manifold SPS-24 (Analytichem International), Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Silica gel for chromatography columns.

5.3.1 Silica Gel for Phenols and Polynuclear Aromatic Hydrocarbons: 100/200 mesh (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow glass tray, loosely covered with foil.

5.3.2 Silica Gel for Organochlorine pesticides/PCBs: 100/200 mesh (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow glass tray, loosely covered with foil. Deactivate it to 3.3% with reagent water in a 500 mL glass jar. Mix the contents thoroughly and allow to equilibrate for 6 hours. Store the deactivated silica gel in a sealed glass jar inside a desiccator.

5.4 Silica cartridges: 40 µm particles, 60 A pores. The cartridges with which this method was developed consist of 6 mL serological-grade polypropylene tubes, with the 1 g of silica held between two polyethylene or stainless steel frits with 20 µm pores. 2 g silica cartridges are also used in this method, and 0.5 g cartridges are available. The compound elution patterns must be verified when cartridges other than the specified size are used.

5.5 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. A method blank must be analyzed in order to demonstrate that there is no interference from the sodium sulfate.

5.6 Eluting solvents

5.6.1 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.6.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.6.3 2-Propanol, $(CH_3)_2CHOH$ - Pesticide quality or equivalent.

5.6.4 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.6.5 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.6 Pentane, C_5H_{12} - Pesticide quality or equivalent.

5.6.7 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.6.8 Diethyl Ether, $C_2H_5OC_2H_5$. Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethanol preservative must be added to each liter of ether.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 General Guidance

7.1.1 The procedure contains two cleanup options for the derivatized phenols and organochlorine pesticides/PCBs, but only one technique for the polynuclear aromatic hydrocarbons (PAHs) (standard column chromatography). Cleanup techniques by standard column chromatography for all analytes are found in Sec. 7.2. Cleanup techniques by solid-phase cartridges for derivatized phenols and PAHs are found in Sec. 7.3. The standard column chromatography techniques are packed with a greater amount of silica gel adsorbent and, therefore, have a greater cleanup capacity. A rule of thumb relating to cleanup capacity is that 1 g of sorbent material will remove 10 to 30 mg of total interferences. (However, capacity is also dependent on the sorbent retentiveness of the interferences.) Therefore, samples that exhibit a greater degree of sample interference should be cleaned up by the standard column technique. However, both techniques have limits on the amount of interference that can be removed. If the interference is caused by high boiling material, then Method 3640 should be used prior to this method. If the interference is caused by relatively polar compounds of the same boiling range as the analytes, then multiple column or cartridge cleanups may be required. If crystals of sulfur are noted in the extract, then Method 3660 should be utilized prior to this method. The cartridge cleanup techniques are often faster and use less solvent, however they have less cleanup capacity.

7.1.2 Allow the extract to reach room temperature if it was in cold storage. Inspect the extracts visually to ensure that there are no particulates or phase separations and that the volume is as stated in the accompanying documents. Verify that the solvent is compatible with the cleanup procedures. If crystals of sulfur are visible or if the presence of sulfur is suspected, proceed with Method 3660.

7.1.3 If the extract solvent is methylene chloride, for most cleanup techniques, it must be exchanged to hexane. (For the PAHs, exchange to cyclohexane as per Sec. 7.2.1). Follow one of the standard concentration techniques provided in each extraction method. The volume of methylene chloride should have been reduced to 1-2 mL. Add 40 mL of hexane, a fresh boiling chip and repeat the concentration as written. The final volume required for the cleanup techniques is normally 2 mL.

7.2 Standard Column Cleanup Techniques

7.2.1 Polynuclear aromatic hydrocarbons

7.2.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. The exchange is performed by adding 4 mL of cyclohexane following reduction of the sample extract to 1-2 mL using an appropriate concentration technique (e.g., K-D using two-ball micro-snyder column) found in the 3500 series methods. The final extract volume is 2.0 mL.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost. If the extract goes to dryness, the extraction must be repeated.

7.2.1.2 Prepare a slurry of 10 g of activated silica gel (Sec. 5.3.1) in methylene chloride and place this into a 10 mm ID chromatographic column. Tap the column to

settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.2.1.3 Pre-elute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

7.2.1.4 Next, elute the column with 25 mL of methylene chloride/pentane (2:3)(v/v) into a flask for concentration. Concentrate the collected fraction to whatever volume is required (1-10 mL). Proceed with HPLC (Method 8310) or GC analysis (Method 8100). Validated components that elute in this fraction are:

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(g,h,i)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

7.2.2 Derivatized Phenols

7.2.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization, as described in Method 8041. The sample extract must be in 2 mL of hexane at this point.

7.2.2.2 Place 4.0 g of activated silica gel (Sec. 5.3.1) into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.2.3 Pre-elute the column with 6 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.2.4 Elute the column, in order, with 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis.

7.2.3 Organochlorine Pesticides and PCBs

7.2.3.1 Transfer a 3 g portion of deactivated silica gel (Sec. 5.3.2) into a 10 mm ID glass chromatographic column and top it with 2 to 3 cm of anhydrous sodium sulfate.

7.2.3.2 Add 10 mL of hexane to the top of the column to wet and rinse the sodium sulfate and silica gel. Just prior to exposure of the sodium sulfate layer to air, stop the hexane eluate flow by closing the stopcock on the chromatographic column. Discard the eluate.

7.2.3.3 Transfer the sample extract (2 mL in hexane) onto the column. Rinse the extract vial twice with 1 to 2 mL of hexane and add each rinse to the column. Elute the column with 80 mL of hexane (Fraction I) at a rate of about 5 mL/min. Remove the collection flask and set it aside for later concentration. Elute the column with 50 mL of hexane (Fraction II) and collect the eluate. Perform a third elution with 15 mL of methylene chloride (Fraction III). The elution patterns for the organochlorine pesticides, Aroclor-1016, and Aroclor-1260 are shown in Table 2.

7.2.3.4 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. Fractions may be combined, as desired, depending upon the specific pesticides/PCBs of interest or level of interferences. Analyze Fraction I containing PCBs separated from most pesticides by Method 8082. Use Method 8081 to analyze for organochlorine pesticides.

7.3 Cartridge Cleanup Techniques

7.3.1 Cartridge Set-up and Conditioning

7.3.1.1 Arrange the 1 g silica cartridges (2 g for phenol cleanup) on the manifold in the closed-valve position. Other size cartridges may be used, however the data presented in the Tables are all based on 1 g cartridges for pesticides/PCBs and 2 g cartridges for phenols. Therefore, supporting recovery data must be developed for other sizes. Larger cartridges will probably require larger volumes of elution solvents.

7.3.1.2 Turn on the vacuum pump and set pump vacuum to 10 inches (254 mm) of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates can be controlled by opening and closing cartridge valves.

7.3.1.3 Condition the cartridges by adding 4 mL of hexane to each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes. Do not turn off the vacuum.

7.3.1.4 Slowly open cartridge valves to allow the hexane to pass through the cartridges. Close the cartridge valves when there is still at least 1 mm of solvent above the sorbent bed. Do not allow cartridges to become dry. If cartridges go dry, repeat the conditioning step.

7.3.2 Derivatized Phenols

7.3.2.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane and the phenols must have undergone derivatization by pentafluorobenzyl bromide, as per the appropriate method.

7.3.2.2 Transfer the extract to the 2 g cartridge that has been conditioned as described in Sec. 7.3.1. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.3.2.3 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vials with an additional 0.5 mL of hexane, and add the rinse to the cartridges to complete the quantitative transfer.

7.3.2.4 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never gets dry.

7.3.2.5 Place a 5 mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align with the collection vial.

7.3.2.6 Add 5 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve, and collect the eluate (this is Fraction 1, and should be discarded).

NOTE: If cartridges smaller than 2 g are used, then Fraction 1 cannot be discarded, since it contains some of the phenols.

7.3.2.7 Close the cartridge valve, replace the collection vial, and add 5 mL of toluene/hexane (25/75, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 2, and should be retained for analysis.

7.3.2.8 Adjust the final volume of the eluant to a known volume which will result in analyte concentrations appropriate for the project requirements (normally 1 - 10 mL) using techniques described in an appropriate 3500 series method. Table 3 shows compound recoveries for 2 g silica cartridges. The cleaned up extracts are ready for analysis by Method 8041.

7.3.3 Organochlorine Pesticides/PCBs

NOTE: The silica cartridge procedure is appropriate when polychlorinated biphenyls are known to be present.

7.3.3.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.3.3.2 Use the 1 g cartridges conditioned as described in Sec. 7.3.1.

7.3.3.3 Transfer the extract to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.3.3.4 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vials with an additional 0.5 mL of solvent, and add the rinse to the cartridges to complete the quantitative transfer.

7.3.3.5 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never goes dry.

7.3.3.6 Place a 5 mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align with the collection vial.

7.3.3.7 Add 5 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial (Fraction 1).

7.3.3.8 Close the cartridge valve, replace the collection vial, and add 5 mL of diethyl ether/hexane (50/50, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial (Fraction 2).

7.3.3.9 Adjust the final volume of each of the two fractions to a known volume which will result in analyte concentrations appropriate for the project requirements (normally 1 - 10 mL) using techniques described in an appropriate 3500 series method. The fractions may be combined prior to final adjustment of volume, if analyte fractionation is not required. Table 4 shows compound recoveries for 1 g silica cartridges. The cleaned up extracts are ready for analysis by Methods 8081 for organochlorine pesticides or 8082 for PCBs.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 A reagent blank (consisting of the elution solvents) must be passed through the column or cartridge and checked for the compounds of interest, prior to the use of this method. This same performance check is required with each new lot of adsorbent or cartridges. The level of interferences must be below the method detection limit before this method is performed on actual samples.

8.3 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples. See the attached Tables for acceptable recovery data. For compounds that have not been tested, recovery must be $\geq$ 85%.

8.3.1 Before any samples are processed using the solid-phase extraction cartridges, the efficiency of the cartridge must be verified. A recovery check must be performed using standards of the target analytes at known concentration. Only lots of cartridges that meet the recovery criteria for the spiked compounds can be used to process the samples.

8.3.2 A check should also be performed on each individual lot of cartridges and for every 300 cartridges of a particular lot.

8.4 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using standard column chromatography.

9.2 Table 2 provides performance information on the fractionation of organochlorine pesticides and Aroclors using standard column chromatography.

9.3 Table 3 shows recoveries of derivatized phenols obtained using 2 g silica cartridges.

9.4 Table 4 shows recoveries and fractionation of organochlorine pesticides obtained using 1 g silica cartridges.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S EPA "Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges," Project Report, December 1989.

TABLE 1

SILICA GEL FRACTIONATION OF PFBBr DERIVATIVES

Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

[a] Eluant composition:

Fraction 1 - 15% toluene in hexane.
Fraction 2 - 40% toluene in hexane.
Fraction 3 - 75% toluene in hexane.
Fraction 4 - 15% 2-propanol in toluene.

Data from Reference 1 (Method 604)

TABLE 2

DISTRIBUTION AND PERCENT RECOVERIES OF ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS IN SILICA GEL COLUMN FRACTIONS[a,b,c,d,e]

Compound	Fraction I		Fraction II		Fraction III		Total Recovery	
	Conc. 1	Conc. 2	Conc. 1	Conc. 2	Conc. 1	Conc. 2	Conc. 1	Conc. 2
alpha-BHC[f]					82(1.7)	74(8.0)	82(1.7)	74(8.0)
beta-BHC					107(2.1)	98(12.5)	107(2.1)	98(12.5)
gamma-BHC					91(3.6)	85(10.7)	91(3.6)	85(10.7)
delta-BHC					92(3.5)	83(10.6)	92(3.5)	83(10.6)
Heptachlor	109(4.1)	118(8.7)					109(4.1)	118(8.7)
Aldrin	97(5.6)	104(1.6)					97(5.6)	104(1.6)
Heptachlor epoxide					95(4.7)	88(10.2)	95(4.7)	88(10.2)
Technical chlordane	14(5.5)	22(5.3)	19(6.8)	39(3.6)	29(5.0)	37(5.1)	62(3.3)	98(1.9)
Endosulfan I					95(5.1)	87(10.2)	95(5.1)	87(10.2)
4,4'-DDE	86(5.4)	94(2.8)					86(5.4)	94(2.8)
Dieldrin					96(6.0)	87(10.6)	96(6.0)	87(10.6)
Endrin					85(10.5)	71(12.3)	85(10.5)	71(12.3)
Endosulfan II					97(4.4)	86(10.4)	97(4.4)	86(10.4)
4,4'-DDD[f]					102(4.6)	92(10.2)	102(4.6)	92(10.2)
Endrin aldehyde					81(1.9)	76(9.5)	81(1.9)	76(9.5)
Endosulfan sulfate					93(4.9)	82(9.2)	93(4.9)	82(9.2)
4,4'-DDT[f]			86(13.4)	73(9.1)	15(17.7)	8.7(15.0)	101(5.3)	82(23.7)
4,4'-Methoxychlor					99(9.9)	82(10.7)	99(9.9)	82(10.7)
Toxaphene[f]			15(2.4)	17(1.4)	73(9.4)	84(10.7)	88(12.0)	101(10.1)
Aroclor-1016	86(4.0)	87(6.1)					86(4.0)	87(6.1)
Aroclor-1260	91(4.1)	95(5.0)					91(4.1)	95(5.0)

TABLE 2
(Continued)

[a] Effluent composition: Fraction I, 80 mL hexane; Fraction II, 50 mL hexane; Fraction III, 15 mL methylene chloride.

[b] Concentration 1 is 0.5 µg per column for BHCs, Heptachlor, Aldrin, Heptachlor epoxide, and Endosulfan I; 1.0 µg per column for Dieldrin, Endosulfan II, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Endrin, Endrin aldehyde, and Endosulfan sulfate; 5 µg per column for 4,4'-Methoxychlor and technical Chlordane; 10 µg per column for Toxaphene, Aroclor-1016, and Aroclor-1260.

[c] For Concentration 2, the amounts spiked are 10 times as high as those for Concentration 1.

[d] Values given represent the average recovery of three determinations; numbers in parentheses are the standard deviation; recovery cutoff point is 5 percent.

[e] Data obtained with standards, as indicated in footnotes b and c, dissolved in 2 mL hexane.

[f] It has been found that because of batch-to-batch variation in the silica gel material, these compounds cross over in two fractions and the amounts recovered in each fraction are difficult to reproduce.

TABLE 3

PERCENT RECOVERIES AND ELUTION PATTERNS FOR 18 PHENOLS FROM 2 g SILICA CARTRIDGES[a]

Compound	Fraction 2 Average Recovery	Percent RSD
Phenol	74.1	5.2
2-Methylphenol	84.8	5.2
3-Methylphenol	86.4	4.4
4-Methylphenol	82.7	5.0
2,4-Dimethylphenol	91.8	5.6
2-Chlorophenol	88.5	5.0
2,6-Dichlorophenol	90.4	4.4
4-Chloro-3-methylphenol	94.4	7.1
2,4-Dichlorophenol	94.5	7.0
2,4,6-Trichlorophenol	97.8	6.6
2,3,6-Trichlorophenol	95.6	7.1
2,4,5-Trichlorophenol	92.3	8.2
2,3,5-Trichlorophenol	92.3	8.2
2,3,5,6-Tetrachlorophenol	97.5	5.3
2,3,4,6-Tetrachlorophenol	97.0	6.1
2,3,4-Trichlorophenol	72.3	8.7
2,3,4,5-Tetrachlorophenol	95.1	6.8
Pentachlorophenol	96.2	8.8

[a] Silica cartridges (Supelco, Inc.) were used; each cartridge was conditioned with 4 mL of hexane prior to use. Each experiment was performed in duplicate at three spiking concentrations (0.05 µg, 0.2 µg, and 0.4 µg per compound per cartridge). Fraction 1 was eluted with 5 mL hexane and was discarded. Fraction 2 was eluted with 5 mL toluene/hexane (25/75, v/v).

Data from Reference 2

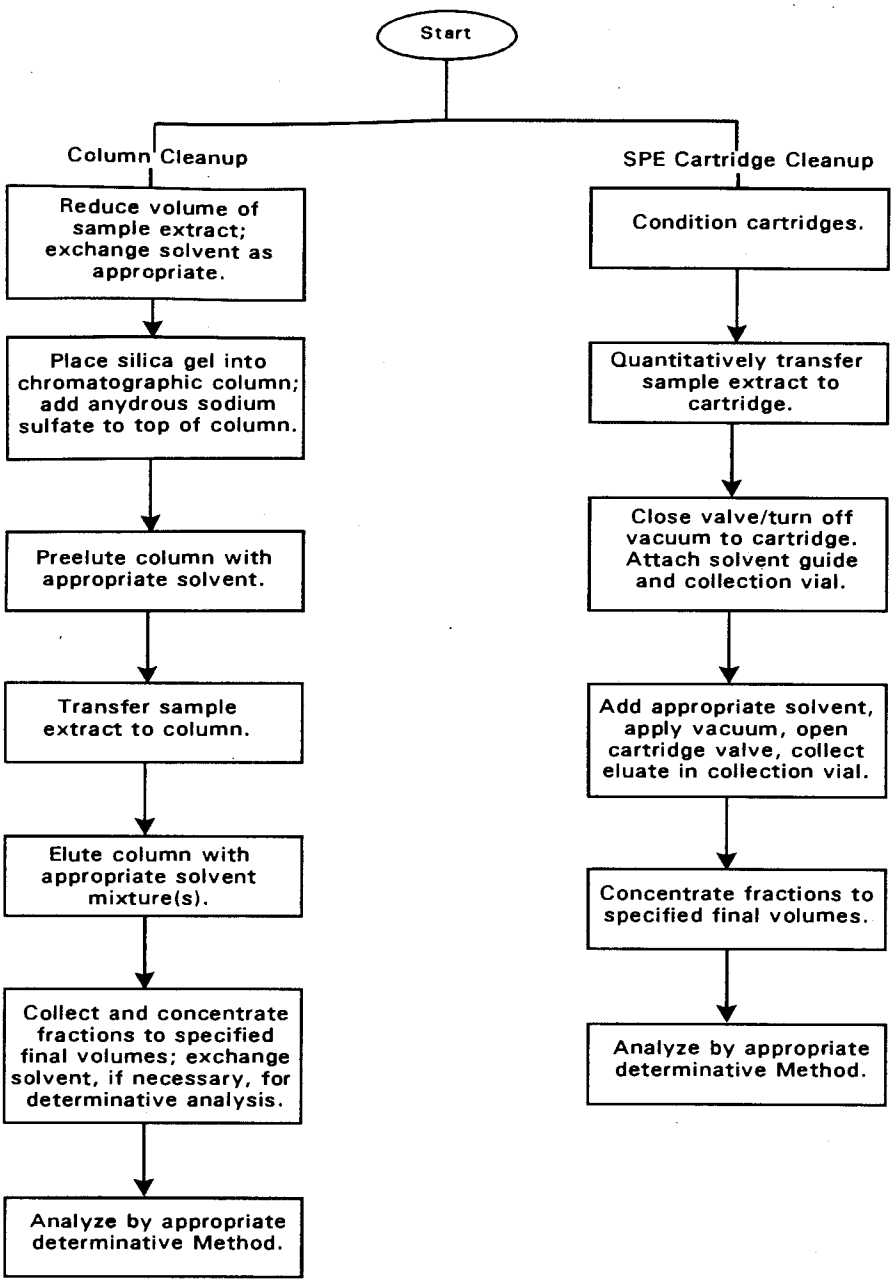
TABLE 4

PERCENT RECOVERIES AND ELUTION PATTERNS FOR 17 ORGANOCHLORINE PESTICIDES AND AROCLORS FROM 1 g SILICA CARTRIDGES[a]

Compound	Fraction 1 Average Recovery	Fraction 1 Percent RSD	Fraction 2 Average Recovery	Fraction 2 Percent RSD
alpha-BHC	0		98.7	2.3
gamma-BHC	0		94.8	1.9
beta-BHC	0		94.3	3.0
Heptachlor	97.3	1.3	0	
delta-BHC	0		90.8	2.5
Aldrin	95.9	1.0	0	
Heptachlor epoxide	0		97.9	2.1
Endosulfan I	0		102	2.3
4,4'-DDE	99.9	1.7	0	
Dieldrin	0		92.3	2.0
Endrin	0		117	2.6
4,4'-DDD	10.7	41	92.4	3.3
Endosulfan II	0		96.0	2.2
4,4'-DDT	94.1	2.0	0	
Endrin aldehyde	0		59.7	2.6
Endosulfan sulfate	0		97.8	2.1
4,4'-Methoxychlor	0		98.0	2.4
Aroclor 1016	124			
Aroclor 1221	93.5			
Aroclor 1232	118			
Aroclor 1242	116			
Aroclor 1248	114			
Aroclor 1254	108			
Aroclor 1264	112			

[a] Silica cartridges (Supelco, Inc. lot SP0161) were used; each cartridge was conditioned with 4 mL hexane prior to use. The organochlorine pesticides were tested separately from PCBs. Each organochlorine pesticides experiment was performed in duplicate, at three spiking concentrations (0.2 µg, 1.0 µg, and 2.0 µg per compound per cartridge). Fraction 1 was eluted with 5 mL of hexane, Fraction 2 with 5 mL of diethyl ether/hexane (50/50, v/v). PCBs were spiked at 10 µg per cartridge and were eluted with 3 mL of hexane. The values given for PCBs are the percent recoveries for a single determination.

Data from Reference 2



Note: Select specific procedures provided in the method depending on the type(s) of analytes of interest. See the method for details regarding the appropriate elution and collection procedures.

METHOD 3640A

GEL-PERMEATION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Gel-permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules (1). The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated (2). A cross-linked divinylbenzene-styrene copolymer (SX-3 Bio Beads or equivalent) is specified for this method.

1.2 General cleanup application - GPC is recommended for the elimination from the sample of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds (2). GPC is appropriate for both polar and non-polar analytes, therefore, it can be effectively used to cleanup extracts containing a broad range of analytes.

1.3 Specific application - This method includes guidance for cleanup of sample extracts containing the following analytes from the RCRA Appendix VIII and Appendix IX lists:

Compound Name	CAS No.[a]
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Acetophenone	98-86-2
2-Acetylaminofluorene	53-96-3
Aldrin	309-00-2
4-Aminobiphenyl	92-67-1
Aniline	62-53-3
Anthracene	120-12-7
Benomyl	17804-35-2
Benzenethiol	108-98-5
Benzidine	92-87-5
Benz(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(a)pyrene	50-32-8
Benzo(ghi)perylene	191-24-2
Benzo(k)fluoranthene	207-08-9
Benzoic acid	65-85-0
Benzotrichloride	98-07-7
Benzyl alcohol	100-51-6
Benzyl chloride	100-44-7
alpha-BHC	319-84-6
beta-BHC	319-85-7

Compound Name	CAS No.[a]
gamma-BHC	58-89-9
delta-BHC	319-86-8
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	88-85-7
Carbazole	86-74-8
Carbendazim	10605-21-7
alpha-Chlordane	5103-71-9
gamma-Chlordane	5566-34-7
4-Chloro-3-methylphenol	59-50-7
4-Chloroaniline	106-47-8
Chlorobenzilate	510-15-6
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	108-60-1
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chlorophenol	106-48-9
3-Chlorophenol	108-43-0
4-Chlorophenyl phenyl ether	7005-72-3
3-Chloropropionitrile	542-76-7
Chrysene	218-01-9
2-Cresol	95-48-7
3-Cresol	108-39-4
4-Cresol	106-44-5
Cyclophosphamide	50-18-0
DDD	72-54-8
DDE	72-55-9
DDT	50-29-3
Di-n-butyl phthalate	84-74-2
Diallate	2303-16-4
Dibenzo(a,e)pyrene	192-65-4
Dibenzo(a,i)pyrene	189-55-9
Dibenz(a,j)acridine	224-42-0
Dibenz(a,h)anthracene	53-70-3
Dibenzofuran	132-64-9
Dibenzothiophene	132-65-0
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
trans-1,4-Dichloro-2-butene	110-57-6
cis-1,4-Dichloro-2-butene	1476-11-5
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	106-46-7
1,4-Dichlorobenzene	541-73-1
3,3'-Dichlorobenzidine	91-94-1
2,6-Dichlorophenol	87-65-0
2,4-Dichlorophenoxyacetic acid (2,4-D)	94-75-7
2,4-Dichlorophenol	120-83-2

Compound Name	CAS No.[a]
2,4-Dichlorotoluene	95-73-8
1,3-Dichloro-2-propanol	96-23-1
Dieldrin	60-57-1
Diethyl phthalate	84-66-2
Dimethoate	60-51-5
Dimethyl phthalate	131-11-3
p-Dimethylaminoazobenzene	60-11-7
7,12-Dimethyl-benz(a)anthracene	57-97-6
2,4-Dimethylphenol	105-67-9
3,3-Dimethylbenzidine	119-93-7
4,6-Dinitro-o-cresol	534-52-1
1,3-Dinitrobenzene	99-65-0
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Diphenylamine	122-39-4
Diphenyl ether	101-84-8
1,2-Diphenylhydrazine	122-66-7
Disulfoton	298-04-4
Endosulfan sulfate	1031-07-8
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Ethyl methane sulfonate	62-50-0
Ethyl methacrylate	97-63-2
Bis(2-ethylhexyl) phthalate	117-81-7
Famphur	52-85-7
Fluorene	86-73-7
Fluoranthene	206-44-0
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Hexachloropropene	1888-71-7
Indeno(1,2,3-cd)pyrene	193-39-5
Isodrin	465-73-6
Isophorone	78-59-1
cis-Isosafrole	17627-76-8
trans-Isosafrole	4043-71-4
Kepone	143-50-0
Malononitrile	109-77-3
Merphos	150-50-5
Methoxychlor	72-43-5
3-Methylcholanthrene	56-49-5

Compound Name	CAS No.[a]
2-Methylnaphthalene	91-57-6
Methyl parathion	298-00-0
4,4'-Methylene-bis(2-chloroaniline)	101-14-4
Naphthalene	91-20-3
1,4-Naphthoquinone	130-15-4
2-Naphthylamine	91-59-8
1-Naphthylamine	134-32-7
5-Nitro-o-toluidine	99-55-8
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6
Nitrobenzene	98-95-3
2-Nitrophenol	79-46-9
4-Nitrophenol	100-02-7
N-Nitrosodi-n-butylamine	924-16-3
N-Nitrosodiethanolamine	1116-54-7
N-Nitrosodiethylamine	55-18-5
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-6
N-Nitrosodi-n-propylamine	621-64-7
N-Nitrosomethylethylamine	10595-95-6
N-Nitrosomorpholine	59-89-2
N-Nitrosopiperidine	100-75-4
N-Nitrosopyrolidine	930-55-2
Di-n-octyl phthalate	117-84-0
Parathion	56-38-2
Pentachlorobenzene	608-93-5
Pentachloroethane	76-01-7
Pentachloronitrobenzene (PCNB)	82-68-8
Pentachlorophenol	87-86-5
Phenacetin	62-44-2
Phenanthrene	85-01-8
Phenol	108-95-2
1,2-Phenylenediamine	95-54-5
Phorate	298-02-2
2-Picoline	109-06-8
Pronamide	23950-58-5
Pyrene	129-00-0
Resorcinol	108-46-3
Safrole	94-59-7
1,2,4,5-Tetrachlorobenzene	95-94-3
2,3,5,6-Tetrachloronitrobenzene	117-18-0
2,3,5,6-Tetrachlorophenol	935-95-5
2,3,4,6-Tetrachlorophenol	58-90-2
Tetraethyl dithiopyrophosphate (Sulfotep)	3689-24-5
Thiosemicarbazide	79-19-6
2-Toluidine	106-49-0
4-Toluidine	95-53-4

Compound Name	CAS No.[a]
Thiourea, 1-(o-chlorophenyl)	5344-82-1
Toluene-2,4-diamine	95-80-7
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
2,4,6-Trichlorophenol	88-06-2
2,4,5-Trichlorophenol	95-95-4
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	93-76-5
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)	93-72-1
Warfarin	81-81-2

[a] Chemical Abstract Services Registry Number.

Table 1 presents average percent recovery and percent RSD data for these analytes, as well as the retention volumes of each analyte on a single GPC system. Retention volumes vary from column to column. Figure 1 provides additional information on retention volumes for certain classes of compounds. The data for the semivolatiles were determined by GC/MS, whereas, the pesticide data were determined by GC/ECD or GC/FPD. Compounds not amenable to GC were determined by HPLC. Other analytes may also be appropriate for this cleanup technique, however, recovery through the GPC should be >70%.

1.4 Normally, this method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph (GC) or the front of the GC column. This residue will ultimately reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. Pentachlorophenol is especially susceptible to this problem. GPC, operating on the principal of size exclusion, will not usually remove interference peaks that appear in the chromatogram since the molecular size of these compounds is relative similar to the target analytes. Separation cleanup techniques, based on other molecular characteristics (i.e., polarity), must be used to eliminate this type of interference.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of preswelled absorbent, and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample extract to be cleaned up. Elution is effected with a suitable solvent(s) and the product is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be analyzed for the compound of interest prior to the use of this method. The level of interferences must be below the estimated quantitation limits (EQLs) of the analytes of interest before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS

4.1 Gel-permeation chromatography system - GPC Autoprep Model 1002 A or B, or equivalent, Analytical Biochemical Laboratories, Inc. Systems that perform very satisfactorily have also been assembled from the following components - an HPLC pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Sec. 7.2.2.

4.1.1 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. (Optional) To simplify switching from the UV detector during calibration to the GPC collection device during extract cleanup, attach a double 3-way valve (Rheodyne Type 50 Teflon Rotary Valve #10-262 or equivalent) so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

4.1.2 Guard column - (Optional) 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319 or equivalent).

4.1.3 Bio Beads (S-X3) - 200-400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent). An additional 5 g of Bio Beads are required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. The UV chromatogram of the Calibration solution should be very similar to that in Figure 2, and the backpressure should be within 6-10 psi. Also, the gel swell ratio in methylene chloride should be in the range of 4.4 - 4.8 mL/g. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

4.1.4 Ultraviolet detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

4.1.5 Strip chart recorder, recording integrator or laboratory data system.

4.1.6 Syringe - 10 mL with Luerlok fitting.

4.1.7 Syringe filter assembly, disposable - Bio-Rad "Prep Disc" sample filter assembly #343-0005, 25 mm, and 5 micron filter discs or equivalent. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

4.2 Analytical balance - 0.0001 g.

4.3 Volumetric flasks, Class A - 10 mL to 1000 mL

4.4 Graduated cylinders

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.1.1 Some brands of methylene chloride may contain unacceptably high levels of acid (HCl). Check the pH by shaking equal portions of methylene chloride and water, then check the pH of the water layer.

5.1.1.1 If the pH of the water layer is $\leq$ 5, filter the entire supply of solvent through a 2 in. x 15 in. glass column containing activated basic alumina. This column should be sufficient for processing approximately 20-30 liters of solvent. Alternatively, find a different supply of methylene chloride.

5.2 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.3 n-Butyl chloride, $CH_3CH_2CH_2CH_2Cl$. Pesticide quality or equivalent.

5.4 GPC Calibration Solution. Prepare a calibration solution in methylene chloride containing the following analytes (in elution order):

Compound	mg/L
corn oil	25,000
bis(2-ethylhexyl) phthalate	1,000
methoxychlor	200
perylene	20
sulfur	80

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

Store the calibration solution in an amber glass bottle with a Teflon lined screw-cap at 4°C, and protect from light. (Refrigeration may cause the corn oil to precipitate. Before use, allow the calibration solution to stand at room temperature until the corn oil dissolves.) Replace the calibration standard solution every 6 months, or more frequently if necessary.

5.5 Corn Oil Spike for Gravimetric Screen. Prepare a solution of corn oil in methylene chloride (5 g/100 mL).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined by the calibration standard will no longer be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 72°F.

7.2 GPC Setup and Calibration

7.2.1 Column Preparation

7.2.1.1 Weigh out 70 g of Bio Beads (SX-3). Transfer them to a quart bottle with a Teflon lined cap or a 500 mL separatory funnel with a large bore stopcock, and add approximately 300 mL of methylene chloride. Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 2 hours. Maintain enough solvent to sufficiently cover the beads at all times. If a guard column is to be used, repeat the above with 5 g of Bio Beads in a 125 mL bottle or a beaker, using 25 mL of methylene chloride.

7.2.1.2 Turn the column upside down from its normal position, and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

7.2.1.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock if one is attached. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

7.2.1.4 Swirl the bead/solvent slurry to get a homogeneous mixture and, if the wetting was done in a quart bottle, quickly transfer it to a 500 mL separatory funnel with a large bore stopcock. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached) and allow the excess solvent to drain. Raise the tube to stop the flow and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

7.2.1.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight

enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

7.2.1.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat Sec. 7.2.1.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is successfully inserted.

7.2.1.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

7.2.1.8 Pack the optional 5 cm column with approximately 5 g of preswelled beads (different guard columns may require different amounts). Connect the guard column to the inlet of the analytical column.

7.2.1.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube will force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel tubing of 1/16" OD x 10/1000" ID x 2". Pump methylene chloride through the column at a rate of 5 mL/min for one hour.

7.2.1.10 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as in Sec. 7.2.1.9) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

7.2.1.11 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant

and the column appears wet. Always recalibrate after column drying has occurred to verify retention volumes have not changed.

7.2.2 Calibration of the GPC Column

7.2.2.1 Using a 10 mL syringe, load sample loop #1 with calibration solution (Sec. 5.6). With the ABC automated system, the 5 mL sample loop requires a minimum of 8 mL of the calibration solution. Use a firm, continuous pressure to push the sample onto the loop. Switch the valve so that GPC flow is through the UV flow-through cell.

7.2.2.2 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace similar to Figure 2 that meets the following requirements. Differences between manufacturers' cell volumes and detector sensitivities may require a dilution of the calibration solution to achieve similar results. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell, and therefore the analytical cell is not acceptable for use.

7.2.2.3 Following are criteria for evaluating the UV chromatogram for column condition.

7.2.2.3.1 Peaks must be observed, and should be symmetrical, for all compounds in the calibration solution.

7.2.2.3.2 Corn oil and phthalate peaks must exhibit >85% resolution.

7.2.2.3.3 Phthalate and methoxychlor peaks must exhibit >85% resolution.

7.2.2.3.4 Methoxychlor and perylene peaks must exhibit >85% resolution.

7.2.2.3.5 Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

7.2.2.3.6 Nitroaromatic compounds are particularly prone to adsorption. For example, 4-nitrophenol recoveries may be low due to a portion of the analyte being discarded after the end of the collection time. Columns should be tested with the semivolatiles matrix spiking solution. GPC elution should continue until after perylene has eluted, or long enough to recover at least 85% of the analytes, whichever time is longer.

7.2.2.4 Calibration for Semivolatiles - Using the information from the UV trace, establish appropriate collect and dump time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of

bis(2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "wash" time of 10 minutes after the elution of sulfur. Each laboratory is required to establish its specific time sequences. See Figure 2 for general guidance on retention time. Figure 1 illustrates retention volumes for different classes of compounds.

7.2.2.5 Calibration for Organochlorine Pesticides/PCBs - Determine the elution times for the phthalate, methoxychlor, perylene, and sulfur. Choose a dump time which removes >85% of the phthalate, but collects >95% of the methoxychlor. Stop collection after the elution of perylene, but before sulfur elutes.

7.2.2.6 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45-55 mL (4.5-5.5 mL/min). If the flow rate is outside of this range, corrective action must be taken, as described above. Once the flow rate is within the range of 4.5-5.5 mL/min, record the column pressure (should be 6-10 psi) and room temperature. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times, and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared. A UV trace that does not meet the criteria in Sec. 7.2.2.3 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

7.2.2.7 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

7.2.2.7.1 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

7.2.2.7.2 The retention times for bis(2-ethylhexyl) phthalate and perylene must not vary more than $\pm$5% between calibrations. If the retention time shift is >5%, take corrective action. Excessive retention time shifts are caused by:

7.2.2.7.2.1 Poor laboratory temperature control or system leaks.

7.2.2.7.2.2 An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.

7.2.2.7.2.3 Excessive laboratory temperatures, causing outgassing of the methylene chloride.

7.2.2.8 Analyze a GPC blank by loading 5 mL of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using a Kuderna-Danish (KD) evaporator. Analyze the concentrate by whatever detectors will be used for the analysis of future samples. Exchange the solvent, if necessary. If the blank exceeds the estimated quantitation limit of the analytes, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping, if necessary.

7.3 Extract Preparation

7.3.1 Adjust the extract volume to 10.0 mL. The solvent extract must be primarily methylene chloride. All other solvents, e.g. 1:1 methylene chloride/acetone, must be concentrated to 1 mL (or as low as possible if a precipitate forms) and diluted to 10.0 mL with methylene chloride. Thoroughly mix the extract before proceeding.

7.3.2 Filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container, e.g. a 15 mL culture tube with a Teflon lined screw cap. Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. The latter is the preferred technique for viscous extracts or extracts with a lot of solids. Particulate larger than 5 microns may scratch the valve, which may result in a system leak and cross-contamination of sample extracts in the sample loops. Repair of the damaged valve is quite expensive.

NOTE: Viscosity of a sample extract should not exceed the viscosity of 1:1 water/glycerol. Dilute samples that exceed this viscosity.

7.4 Screening the Extract

7.4.1 Screen the extract to determine the weight of dissolved residue by evaporating a 100 µL aliquot to dryness and weighing the residue. The weight of dissolved residue loaded on the GPC column cannot exceed 0.500 g. Residues exceeding 0.500 g will very likely result in incomplete extract cleanup and contamination of the GPC switching valve (which results in cross-contamination of sample extracts).

7.4.1.1 Transfer 100 µL of the filtered extract from Sec. 7.3.2 to a tared aluminum weighing dish.

7.4.1.2 A suggested evaporation technique is to use a heat lamp. Set up a 250 watt heat lamp in a hood so that it is 8 $\pm$ 0.5 cm from a surface covered with a clean sheet of aluminum foil. Surface temperature should be 80-100°C (check temperature by placing a thermometer on the foil and under the lamp). Place the

weighing dish under the lamp using tongs. Allow it to stay under the lamp for 1 min. Transfer the weighing dish to an analytical balance or a micro balance and weigh to the nearest 0.1 mg. If the residue weight is less than 10 mg/100 µL, then further weighings are not necessary. If the residue weight is greater than 10 mg/100 µL, then determine if constant weight has been achieved by placing the weighing dish and residue back under the heat lamp for 2 or more additional 0.5 min. intervals. Reweigh after each interval. Constant weight is achieved when three weights agree within ±10%.

7.4.1.3 Repeat the above residue analysis on a blank and a spike. Add 100 µL of the same methylene chloride used for the sample extraction to a weighing dish and determine residue as above. Add 100 µL of a corn oil spike (5 g/100 mL) to another weighing dish and repeat the residue determination.

7.4.2 A residue weight of 10 mg/100 µL of extract represents 500 mg in 5 mL of extract. Any sample extracts that exceed the 10 mg/100 µL residue weight must be diluted so that the 5 mL loaded on the GPC column does not exceed 0.500 g. When making the dilution, keep in mind that a minimum volume of 8 mL is required when loading the ABC GPC unit. Following is a calculation that may be used to determine what dilution is necessary if the residue exceeds 10 mg.

$$\text{Y mL taken for dilution} = \text{10 mL final volume} \times \frac{\text{10 mg maximum}}{\text{X mg of residue}}$$

Example:

$$\text{Y mL taken for dilution} = \text{10 mL final volume} \times \frac{\text{10 mg maximum}}{\text{15 mg of residue}}$$

Y mL taken for dilution = 6.7 mL

Therefore, taking 6.7 mL of sample extract from Sec. 7.3.2, and diluting to 10 mL with methylene chloride, will result in 5 mL of diluted extract loaded on the GPC column that contains 0.500 g of residue.

NOTE: This dilution factor must be included in the final calculation of analyte concentrations. In the above example, the dilution factor is 1.5.

7.5 GPC Cleanup

7.5.1 Calibrate the GPC at least once per week following the procedure outlined in Secs. 7.2.2 through 7.2.2.6. Ensure that UV trace requirements, flow rate and column pressure criteria are acceptable. Also, the retention time shift must be <5% when compared to retention times in the last calibration UV trace.

7.5.1.1 If these criteria are not met, try cleaning the column by loading one or more 5 mL portions of butyl chloride and running it through the column. Butyl chloride or 9:1 (v/v)

methylene chloride/methanol removes the discoloration and particulate that may have precipitated out of the methylene chloride extracts. Backflushing (reverse flow) with methylene chloride to dislodge particulates may restore lost resolution. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore acceptable performance, the column must be repacked with new Bio Beads and calibrated.

7.5.2 Draw a minimum of 8 mL of extract (diluted, if necessary, and filtered) into a 10 mL syringe.

7.5.3 Attach the syringe to the turn lock on the injection port. Use firm, continuous pressure to push the sample onto the 5-mL sample loop. If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action. If the back pressure is normal (6-10 psi), the blockage is probably in the valve. Blockage may be flushed out of the valve by reversing the inlet and outlet tubes and pumping solvent through the tubes. (This should be done before sample loading.)

NOTE: Approximately 2 mL of the extract remains in the lines between the injection port and the sample loop; excess sample also passes through the sample loop to waste.

7.5.4 After loading a loop, and before removing the syringe from the injection port, index the GPC to the next loop. This will prevent loss of sample caused by unequal pressure in the loops.

7.5.5 After loading each sample loop, wash the loading port with methylene chloride in a PTFE wash bottle to minimize cross-contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

7.5.6 After loading all the sample loops, index the GPC to the OO position, switch to the "RUN" mode and start the automated sequence. Process each sample using the collect and dump cycle times established in Sec. 7.2.2.

7.5.7 Collect each sample in a 250 mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a Kuderna-Danish evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

7.5.7.1 Change in solvent flow rate, caused by channeling in the column or changes in column pressure.

7.5.7.2 Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.

7.5.7.3 Leaks in the system or significant variances in room temperature.

7.6 Concentrate the extract by the standard K-D technique (see any of the extraction methods, Sec. 4.2.1 of this chapter). See the determinative methods (Chapter Four, Sec. 4.3) for the final volume.

7.7 It should be remembered that only half of the sample extract is processed by the GPC (5 mL of the 10 mL extract is loaded onto the GPC column), and thus, a dilution factor of 2 (or 2 multiplied by any dilution factor in Sec. 7.4.2) must be used for quantitation of the sample in the determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 3600 for specific quality control procedures.

8.2 The analyst should demonstrate that the compound(s) of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for single laboratory performance data.

10.0 REFERENCES

1. Wise, R.H.; Bishop, D.F.; Williams, R.T.; Austern, B.M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges"; U.S. EPA Municipal Environmental Research Laboratory: Cincinnati, Ohio 45268.

2. Czuczwa, J.; Alford-Stevens, A. "Optimized Gel Permeation Chromatographic Cleanup for Soil, Sediment, Waste and Waste Oil Sample Extracts for GC/MS Determination of Semivolatile Organic Pollutants, JAOAC, submitted April 1989.

3. Marsden, P.J.; Taylor, V.; Kennedy, M.R. "Evaluation of Method 3640 Gel Permeation Cleanup"; Contract No. 68-03-3375, U.S. Environmental Protection Agency, Cincinnati, Ohio, pp. 100, 1987.

TABLE 1
GPC RECOVERY AND RETENTION VOLUMES FOR RCRA
APPENDIX VIII ANALYTES

Compound	% Rec[1]	% RSD[2]	Ret. Vol.[3] (mL)
Acenaphthene	97	2	196-235
Acenaphthylene	72	10	196-235
Acetophenone	94	7	176-215
2-Acetylaminofluorene	97	2	156-195
Aldrin	99	9	196-215
4-Aminobiphenyl	96	7	176-215
Aniline	93	4	196-235
Anthracene	89	2	196-235
Benomyl	131	8	146-195
Benzenethiol	92	11	196-235
Benzidine	95	5	176-215
Benz(a)anthracene	100	3	196-235
Benzo(b)fluoranthene	93	5	196-235
Benzo(a)pyrene	93	3	196-235
Benzo(ghi)perylene	90	6	196-235
Benzo(k)fluoranthene	91	4	196-235
Benzoic acid	66	7	176-195
Benzotrichloride	93	7	176-215
Benzyl alcohol	95	17	176-215
Benzyl chloride	99	4	176-215
alpha-BHC	84	13	196-215
beta-BHC	94	9	196-215
gamma-BHC	93	4	196-215
delta-BHC	102	7	216-255
4-Bromophenyl phenyl ether	93	1	176-215
Butyl benzyl phthalate	104	3	136-175
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	103	18	176-195
Carbazole	99	5	196-255
Carbendazim	131	8	146-195
alpha-Chlordane	97	2	196-235
gamma-Chlordane	93	2	196-215
4-Chloro-3-methylphenol	87	1	196-255
4-Chloroaniline	88	3	196-235
Chlorobenzilate	92	5	176-235
Bis(2-chloroethoxy)methane	89	1	156-195
Bis(2-chloroethyl) ether	76	2	156-215
Bis(2-chloroisopropyl) ether	83	2	156-195
2-Chloronaphthalene	89	1	196-235
2-Chlorophenol	90	1	196-215
3-Chlorophenol	86	3	196-215
4-Chlorophenol	87	2	196-215
4-Chlorophenyl phenyl ether	98	2	176-215
3-Chloropropionitrile	80	5	176-215
Chrysene	102	1	196-235
2-Cresol	91	1	196-215

TABLE 1 (continued)

Compound	% Rec[1]	%RSD[2]	Ret. Vol.[3] (mL)
3-Cresol	70	3	196-215
4-Cresol	88	2	196-215
Cyclophosphamide	114	10	146-185
DDD	94	4	196-235
DDE	94	2	196-235
DDT	96	6	176-215
Di-n-butyl phthalate	104	3	136-175
Diallate	97	6	156-175
Dibenzo(a,e)pyrene	94	10	216-235
Dibenzo(a,i)pyrene	99	8	216-235
Dibenz(a,j)acridine	117	9	176-195
Dibenz(a,h)anthracene	92	5	196-235
Dibenzofuran	94	1	176-235
Dibenzothiophene	94	3	196-235
1,2-Dibromo-3-chloropropane	83	2	176-215
1,2-Dibromoethane	121	8	196-215
trans-1,4-Dichloro-2-butene	107	6	176-195
cis-1,4-Dichloro-2-butene	106	6	176-215
1,2-Dichlorobenzene	81	1	196-235
1,3-Dichlorobenzene	81	1	196-235
1,4-Dichlorobenzene	81	1	196-235
3,3'-Dichlorobenzidine	98	3	176-215
2,6-Dichlorophenol	86	3	196-215
2,4-Dichlorophenoxyacetic acid (2,4-D)	80	NA	176-215
2,4-Dichlorophenol	87	2	96-215
2,4-Dichlorotoluene	70	9	196-235
1,3-Dichloro-2-propanol	73	13	176-215
Dieldrin	100	5	196-215
Diethyl phthalate	103	3	136-195
Dimethoate	79	15	146-185
3,3'-Dimethoxybenzidine[a]	15	11	156-195
Dimethyl phthalate	100	1	156-195
p-Dimethylaminoazobenzene	96	1	176-215
7,12-Dimethyl-benz(a)anthracene	77	1	176-215
2,4-Dimethylphenol	93	2	176-215
3,3'-Dimethylbenzidine	93	2	156-215
4,6-Dinitro-o-cresol	100	1	156-195
1,3-Dinitrobenzene	99	2	156-195
2,4-Dinitrophenol	118	7	176-195
2,4-Dinitrotoluene	93	4	156-195
2,6-Dinitrotoluene	101	2	156-175
Diphenylamine	95	6	176-235
Diphenyl ether	67	12	196-215
1,2-Diphenylhydrazine	92	1	176-215
Disulfoton	81	15	146-165
Endosulfan sulfate	94	2	176-195
Endosulfan I	99	8	176-215

TABLE 1 (continued)

Compound	% Rec[1]	%RSD[2]	Ret. Vol.[3] (mL)
Endosulfan II	92	6	196-215
Endrin	95	6	196-215
Endrin aldehyde	97	1	176-215
Endrin ketone	94	4	176-215
Ethyl methane sulfonate	62	7	176-235
Ethyl methacrylate	126	7	176-195
Bis(2-ethylhexyl) phthalate	101	1	120-145
Famphur	99	NA	126-165
Fluorene	95	1	176-235
Fluoranthene	94	1	196-235
Heptachlor	85	2	195-215
Heptachlor epoxide	91	11	156-195
Hexachlorobenzene	108	2	196-235
Hexachlorobutadiene	86	2	176-215
Hexachlorocyclopentadiene	89	3	176-215
Hexachloroethane	85	1	196-235
Hexachloropropene	91	2	196-235
Indeno(1,2,3-cd)pyrene	79	13	216-255
Isodrin	98	5	196-235
Isophorone	68	7	156-195
cis-Isosafrole	90	4	176-215
trans-Isosafrole	88	16	156-195
Kepone	102	NA	196-235
Malononitrile	111	9	156-195
Merphos	93	12	126-165
Methoxychlor	94	6	156-195
3-Methylcholanthrene	74	12	176-195
2-Methylnaphthalene	67	6	196-215
Methyl parathion	84	13	146-185
4,4'-Methylene-bis(2-chloroaniline)	96	1	176-215
Naphthalene	95	7	196-215
1,4-Naphthoquinone	73	7	176-215
2-Naphthylamine	94	8	196-235
1-Naphthylamine	96	6	196-235
5-Nitro-o-toluidine	77	2	176-195
2-Nitroaniline	96	8	176-215
3-Nitroaniline	96	2	176-215
4-Nitroaniline	103	8	176-215
Nitrobenzene	86	2	176-195
2-Nitrophenol	95	3	176-195
4-Nitrophenol	77	3	196-215
N-Nitroso-di-n-butylamine	89	4	156-175
N-Nitrosodiethanolamine	104	3	146-185
N-Nitrosodiethylamine	94	2	156-175
N-Nitrosodimethylamine	86	13	156-195
N-Nitrosodiphenylamine	99	2	156-195
N-Nitrosodi-n-propylamine	85	4	156-175

TABLE 1 (continued)

Compound	% Rec[1]	%RSD[2]	Ret. Vol.[3] (mL)
N-Nitrosomethylethylamine	83	7	156-175
N-Nitrosomorpholine	86	4	156-195
N-Nitrosopiperidine	84	4	156-195
N-Nitrosopyrolidine	92	1	156-175
Di-n-octyl phthalate	83	4	120-156
Parathion	109	14	146-170
Pentachlorobenzene	95	2	196-235
Pentachloroethane	74	1	196-235
Pentachloronitrobenzene (PCNB)	91	8	156-195
Pentachlorophenol	102	1	196-215
Phenacetin	100	3	156-195
Phenanthrene	94	2	196-235
Phenol	83	2	156-195
1,2-Phenylenediamine	91	1	196-215
Phorate	74	NA	116-135
2-Picoline	99	14	156-215
Pronamide	105	15	156-195
Pyrene	98	2	215-235
Resorcinol	70	6	196-215
Safrole	93	1	176-215
Streptozotocin[a]	6	48	225-245
1,2,4,5-Tetrachlorobenzene	96	2	196-235
2,3,5,6-Tetrachloro-nitrobenzene	85	9	176-215
2,3,4,6-Tetrachlorophenol	95	1	196-215
2,3,5,6-Tetrachlorophenol	96	7	196-215
Tetraethyl dithiopyrophosphate (Sulfotep)	89	14	116-135
Thiosemicarbazide	74	3	146-185
2-Toluidine	92	3	176-235
4-Toluidine	87	8	176-235
Thiourea, 1-(o-chlorophenyl)	75	11	166-185
Toluene-2,4-diamine	69	7	176-215
1,2,3-Trichlorobenzene	87	1	196-235
1,2,4-Trichlorobenzene	89	1	196-235
2,4,5-Trichlorophenol	77	1	216-235
2,4,6-Trichlorophenol	95	1	216-235
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	71	23	156-235
2,4,5-Trichlorophenoxypropionic acid	67	NA	216-215
Warfarin	94	2	166-185

NA = Not applicable, recovery presented as the average of two determinations.

[a] Not an appropriate analyte for this method.

[1] The percent recovery is based on an average of three recovery values.

[2] The % relative standard deviation is determined from three recovery values.

[3] These Retention Volumes are for guidance only as they will differ from column to column and from system to system.

Figure 1
GPC RETENTION VOLUME OF CLASSES OF ANALYTES

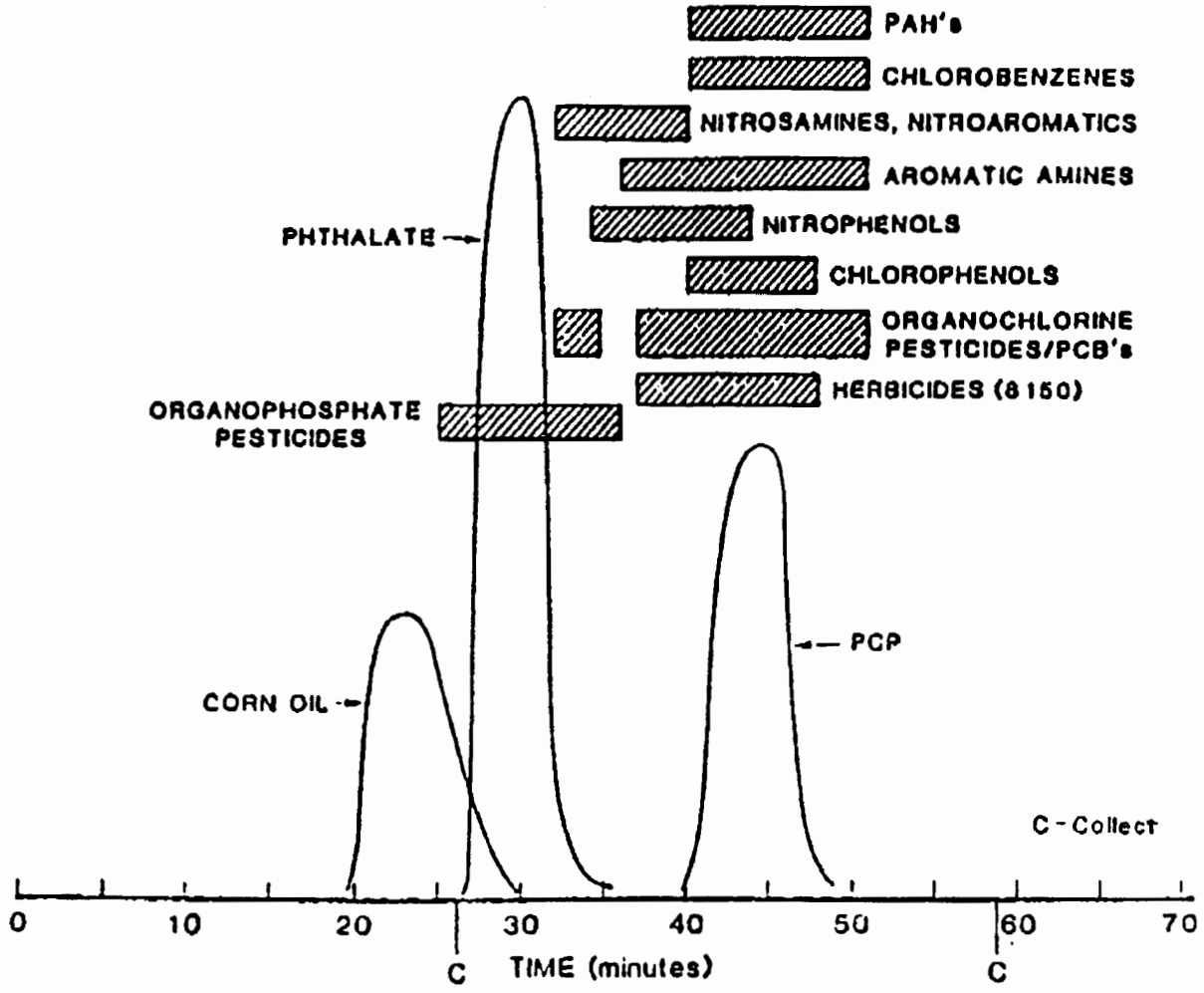
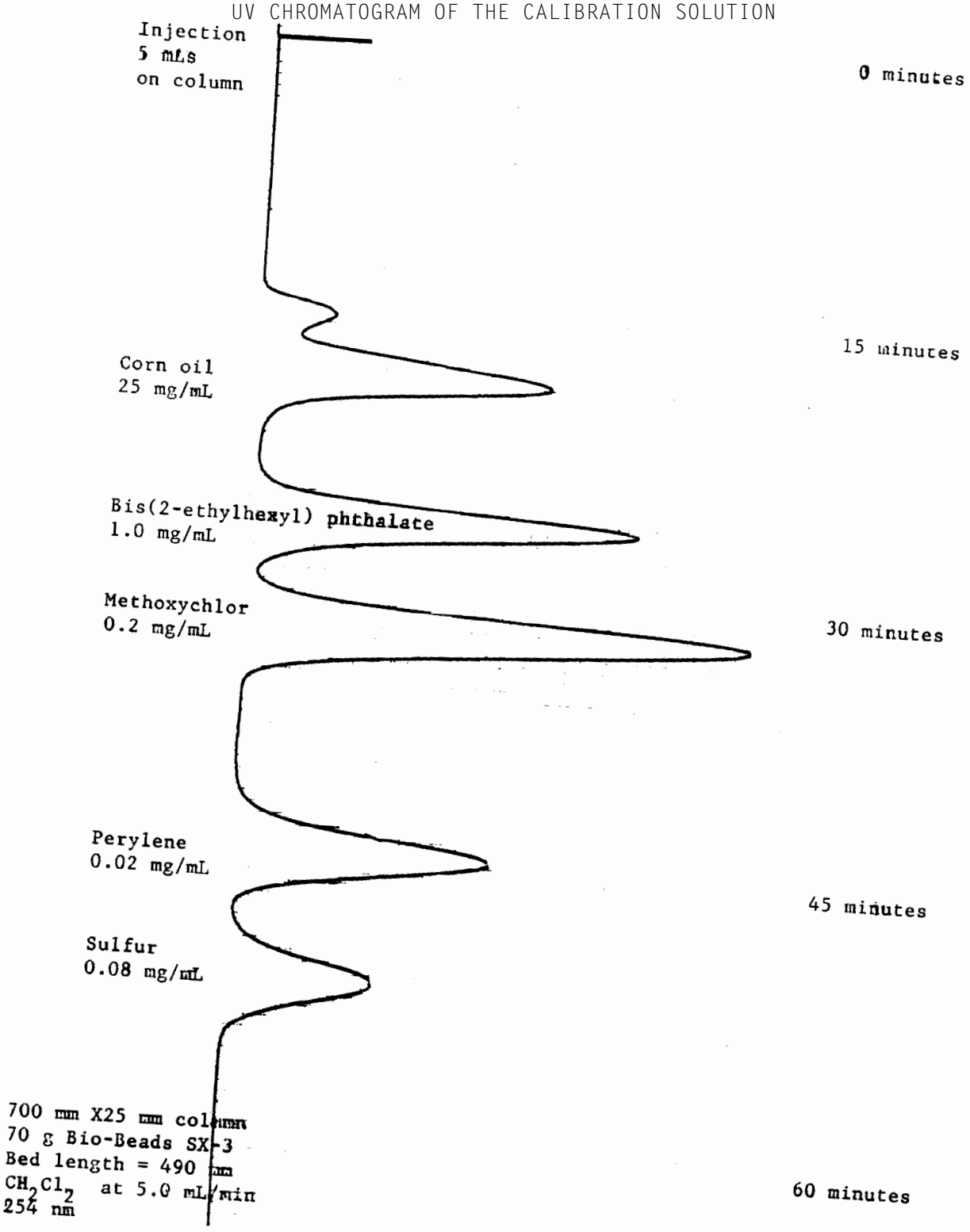
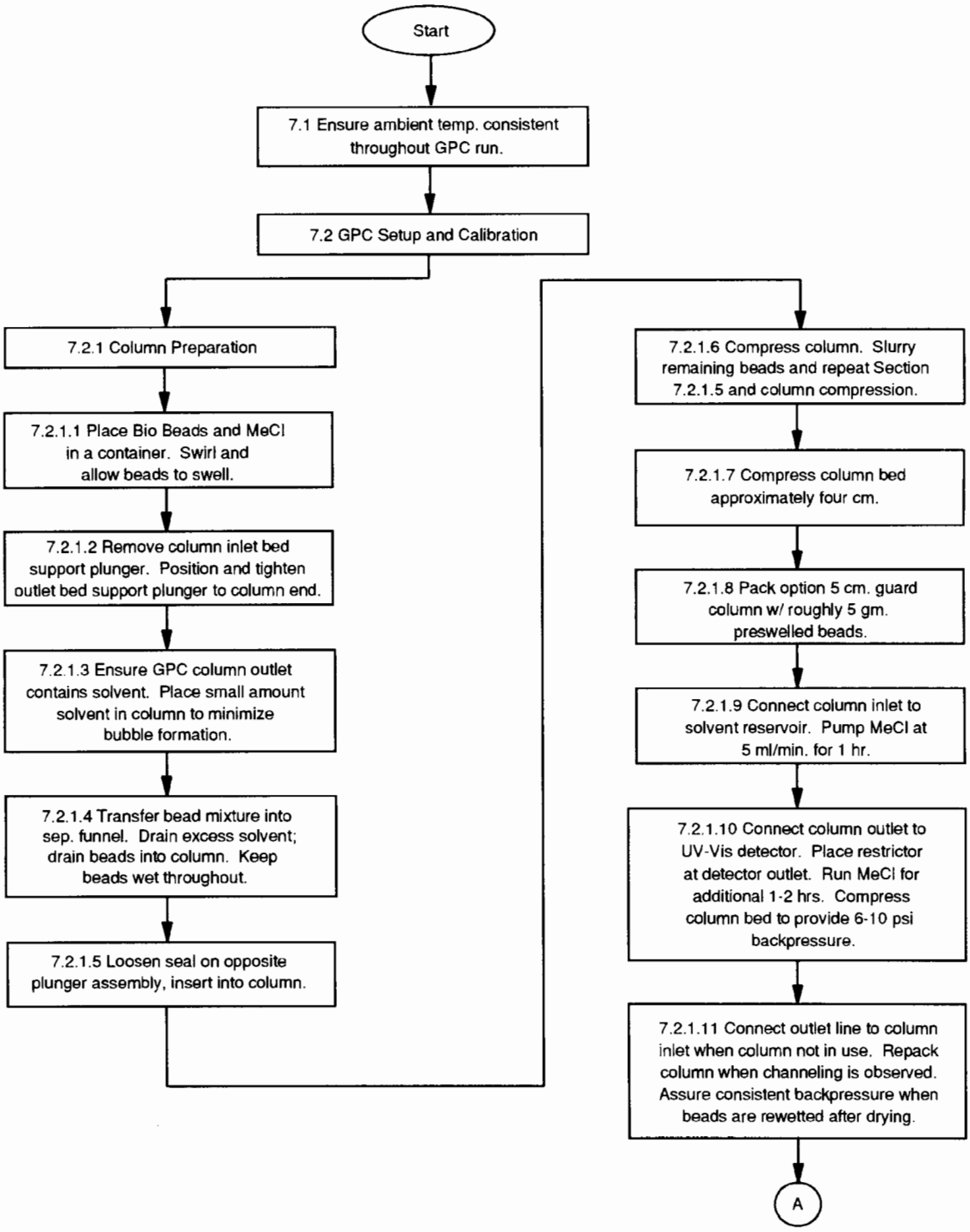
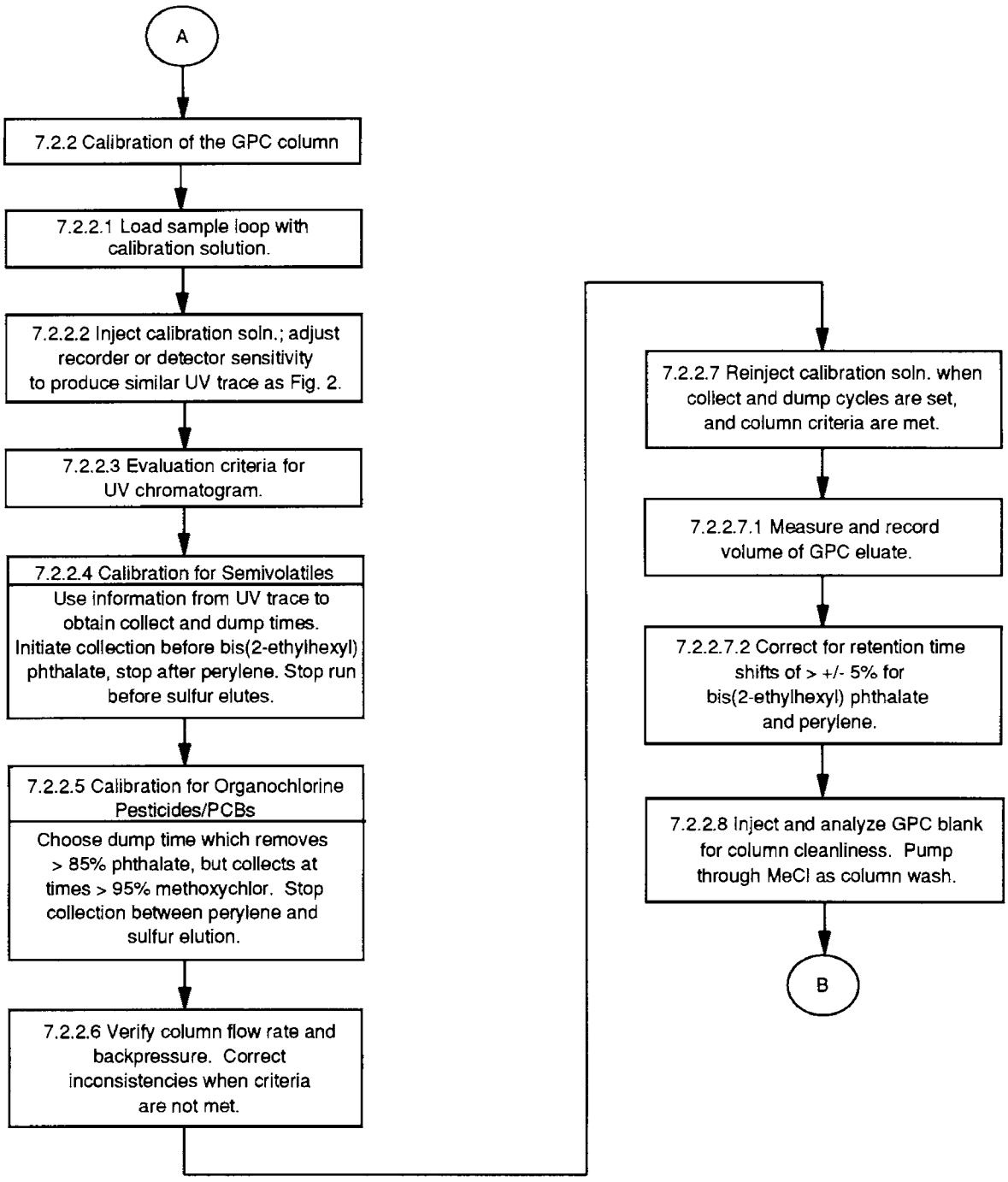
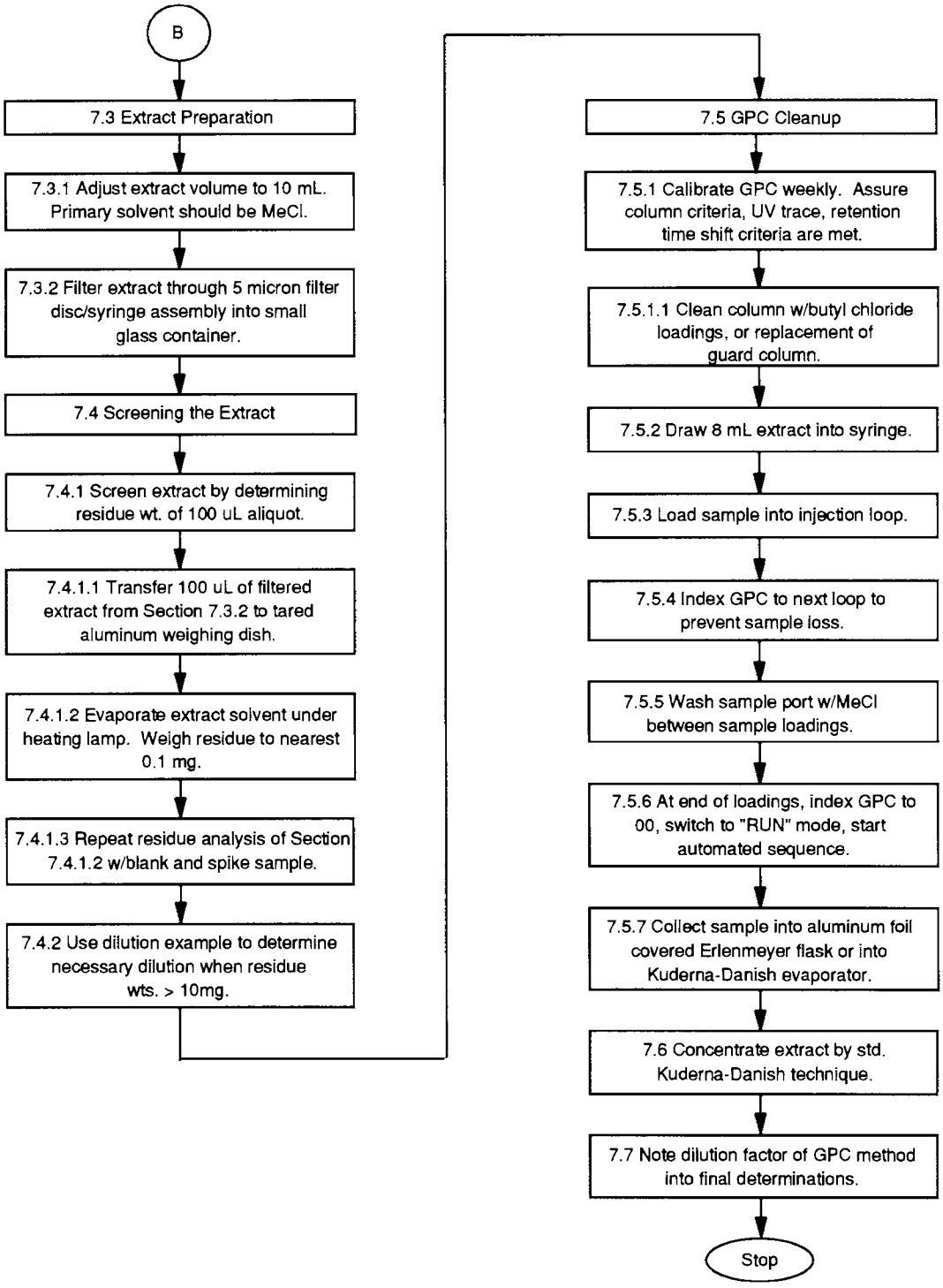


Figure 2
UV CHROMATOGRAM OF THE CALIBRATION SOLUTION




Start
7.1 Ensure ambient temp. consistent throughout GPC run.
7.2 GPC Setup and Calibration
7.2.1 Column Preparation
7.2.1.1 Place Bio Beads and MeCl in a container. Swirl and allow beads to swell.
7.2.1.2 Remove column inlet bed support plunger. Position and tighten outlet bed support plunger to column end.
7.2.1.3 Ensure GPC column outlet contains solvent. Place small amount solvent in column to minimize bubble formation.
7.2.1.4 Transfer bead mixture into sep. funnel. Drain excess solvent; drain beads into column. Keep beads wet throughout.
7.2.1.5 Loosen seal on opposite plunger assembly, insert into column.
7.2.1.6 Compress column. Slurry remaining beads and repeat Section 7.2.1.5 and column compression.
7.2.1.7 Compress column bed approximately four cm.
7.2.1.8 Pack option 5 cm. guard column w/ roughly 5 gm. preswelled beads.
7.2.1.9 Connect column inlet to solvent reservoir. Pump MeCl at 5 ml/min. for 1 hr.
7.2.1.10 Connect column outlet to UV-Vis detector. Place restrictor at detector outlet. Run MeCl for additional 1-2 hrs. Compress column bed to provide 6-10 psi backpressure.
7.2.1.11 Connect outlet line to column inlet when column not in use. Repack column when channeling is observed. Assure consistent backpressure when beads are rewetted after drying.
A


A
7.2.2 Calibration of the GPC column
7.2.2.1 Load sample loop with calibration solution.
7.2.2.2 Inject calibration soln.; adjust recorder or detector sensitivity to produce similar UV trace as Fig. 2.
7.2.2.3 Evaluation criteria for UV chromatogram.
7.2.2.4 Calibration for Semivolatiles
Use information from UV trace to obtain collect and dump times. Initiate collection before bis(2-ethylhexyl) phthalate, stop after perylene. Stop run before sulfur elutes.
7.2.2.5 Calibration for Organochlorine Pesticides/PCBs
Choose dump time which removes > 85% phthalate, but collects at times > 95% methoxychlor. Stop collection between perylene and sulfur elution.
7.2.2.6 Verify column flow rate and backpressure. Correct inconsistencies when criteria are not met.
7.2.2.7 Reinject calibration soln. when collect and dump cycles are set, and column criteria are met.
7.2.2.7.1 Measure and record volume of GPC eluate.
7.2.2.7.2 Correct for retention time shifts of > +/- 5% for bis(2-ethylhexyl) phthalate and perylene.
7.2.2.8 Inject and analyze GPC blank for column cleanliness. Pump through MeCl as column wash.
B


B
7.3 Extract Preparation
7.3.1 Adjust extract volume to 10 mL. Primary solvent should be MeCl.
7.3.2 Filter extract through 5 micron filter disc/syringe assembly into small glass container.
7.4 Screening the Extract
7.4.1 Screen extract by determining residue wt. of 100 uL aliquot.
7.4.1.1 Transfer 100 uL of filtered extract from Section 7.3.2 to tared aluminum weighing dish.
7.4.1.2 Evaporate extract solvent under heating lamp. Weigh residue to nearest 0.1 mg.
7.4.1.3 Repeat residue analysis of Section 7.4.1.2 w/blank and spike sample.
7.4.2 Use dilution example to determine necessary dilution when residue wts. > 10mg.
7.5 GPC Cleanup
7.5.1 Calibrate GPC weekly. Assure column criteria, UV trace, retention time shift criteria are met.
7.5.1.1 Clean column w/butyl chloride loadings, or replacement of guard column.
7.5.2 Draw 8 mL extract into syringe.
7.5.3 Load sample into injection loop.
7.5.4 Index GPC to next loop to prevent sample loss.
7.5.5 Wash sample port w/MeCl between sample loadings.
7.5.6 At end of loadings, index GPC to 00, switch to "RUN" mode, start automated sequence.
7.5.7 Collect sample into aluminum foil covered Erlenmeyer flask or into Kuderna-Danish evaporator.
7.6 Concentrate extract by std. Kuderna-Danish technique.
7.7 Note dilution factor of GPC method into final determinations.
Stop

METHOD 3650B

ACID-BASE PARTITION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3650 is a liquid-liquid partitioning cleanup method to separate acid analytes, e.g., organic acids and phenols, from base/neutral analytes, e.g. amines, aromatic hydrocarbons, and halogenated organic compounds, using pH adjustment. It may be used for cleanup of petroleum waste prior to analysis or further cleanup (e.g., alumina cleanup). The following compounds can be separated by this method:

Compound Name	CAS No.[a]	Fraction
Benz(a)anthracene	56-55-3	Base-neutral
Benzo(a)pyrene	50-32-8	Base-neutral
Benzo(b)fluoranthene	205-99-2	Base-neutral
Chlordane	57-74-9	Base-neutral
Chlorinated dibenzodioxins		Base-neutral
2-Chlorophenol	95-57-8	Acid
Chrysene	218-01-9	Base-neutral
Creosote	8001-58-9	Base-neutral and Acid
Cresol(s)		Acid
Dichlorobenzene(s)		Base-neutral
Dichlorophenoxyacetic acid	94-75-7	Acid
2,4-Dimethylphenol	105-67-9	Acid
Dinitrobenzene	25154-54-5	Base-neutral
4,6-Dinitro-o-cresol	534-52-1	Acid
2,4-Dinitrotoluene	121-14-2	Base-neutral
Heptachlor	76-44-8	Base-neutral
Hexachlorobenzene	118-74-1	Base-neutral
Hexachlorobutadiene	87-68-3	Base-neutral
Hexachloroethane	67-72-1	Base-neutral
Hexachlorocyclopentadiene	77-47-4	Base-neutral
Naphthalene	91-20-3	Base-neutral
Nitrobenzene	98-95-3	Base-neutral
4-Nitrophenol	100-02-7	Acid
Pentachlorophenol	87-86-5	Acid
Phenol	108-95-2	Acid
Phorate	298-02-2	Base-neutral
2-Picoline	109-06-8	Base-neutral
Pyridine	110-86-1	Base-neutral
Tetrachlorobenzene(s)		Base-neutral
Tetrachlorophenol(s)		Acid
Toxaphene	8001-35-2	Base-neutral
Trichlorophenol(s)		Acid
2,4,5-TP (Silvex)	93-72-1	Acid

[a] Chemical Abstract Service Registry Number.

1.2 Method 3650 was formerly Method 3530 in the second edition of this manual.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The solvent extract from a prior solvent extraction method is shaken with water that is strongly basic. The acid analytes partition into the aqueous layer, whereas, the basic and neutral compounds stay in the organic solvent. The base/neutral fraction is concentrated and is then ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated (if necessary) and is then ready for analysis of the acid analytes.

3.0 INTERFERENCES

3.1 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.2 A method blank must be run for the compounds of interest prior to use of the method. The interferences must be below the method detection limit before this method is applied to actual samples.

4.0 APPARATUS AND MATERIALS

4.1 Drying column - 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom, or equivalent.

NOTE: Fritted glass discs are difficult to clean after highly contaminated extracts have been passed through them. Columns without frits are recommended. Use a small pad of Pyrex® glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Vials - Glass, 2 mL capacity with polytetrafluoroethylene (PTFE)-lined screw-caps or crimp tops.

4.3 Water bath - Heated, concentric ring cover, temperature control of ± 2°C. Use this bath in a hood.

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 pH indicator paper - pH range including the desired extraction pH.

4.6 Separatory funnel - 125 mL.

4.7 Erlenmeyer flask - 125 mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide, NaOH, (10N) - Dissolve 40 g of sodium hydroxide in 100 mL of organic-free reagent water.

5.4 Sulfuric acid, H_2SO_4, (1:1 v/v in water) - Slowly add 50 mL H_2SO_4 to 50 mL of organic-free reagent water.

5.5 Sodium sulfate (granular, anhydrous), Na_2SO_4 - Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.6 Solvents:

5.6.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.6.3 Methanol, CH_3OH - Pesticide quality or equivalent.

5.6.4 Diethyl Ether, $C_2H_5OC_2H_5$ - Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

7.2 Add 20 mL of methylene chloride to the separatory funnel.

7.3 Slowly add 20 mL of prechilled organic-free reagent water which has been previously adjusted to a pH of 12-13 with 10N sodium hydroxide.

7.4 Seal and shake the separatory funnel for at least 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to prevent unnecessary exposure of the analyst to the organic vapor.

7.5 Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

7.6 Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using 20 mL aliquots of dilute sodium hydroxide (pH 12-13). Combine the aqueous extracts.

7.7 Water soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase, discard the methylene chloride and proceed to Sec. 7.8. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Sec. 7.10.

7.8 Externally cool the 125 mL Erlenmeyer flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Quantitatively transfer the cool aqueous phase to a clean 125 mL separatory funnel. Add 20 mL of methylene chloride to the separatory funnel and shake for at least 2 minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask.

7.9 Add 20 mL of methylene chloride to the separatory funnel and extract at pH 1-2 a second time. Perform a third extraction in the same manner combining the extracts in the Erlenmeyer flask.

7.10 Prepare a concentration apparatus (if necessary). Refer to the 3500 series methods for guidance regarding concentration of samples.

7.11 Dry both acid and base/neutral fractions by passing them through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried fractions in concentrator container. Rinse the Erlenmeyer flasks which contained the solvents and the columns with 20 mL of methylene chloride to complete the quantitative transfer.

7.12 The acid fraction is now ready for analysis. If the base/neutral fraction requires further cleanup by the alumina column cleanup for petroleum waste (Method 3611), the solvent may have to be changed to hexane. If a solvent exchange is required, add approximately 5 mL of the exchange solvent to the fraction before concentration. Concentrate the fractions to the final volume (usually 1 mL) listed in the appropriate determinative method using the techniques described in an appropriate 3500 series method. If no further cleanup of the base/neutral extract is required, the fraction is ready for analysis.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for general quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For samples that are cleaned using this method, the associated quality control samples must be processed through this cleanup method.

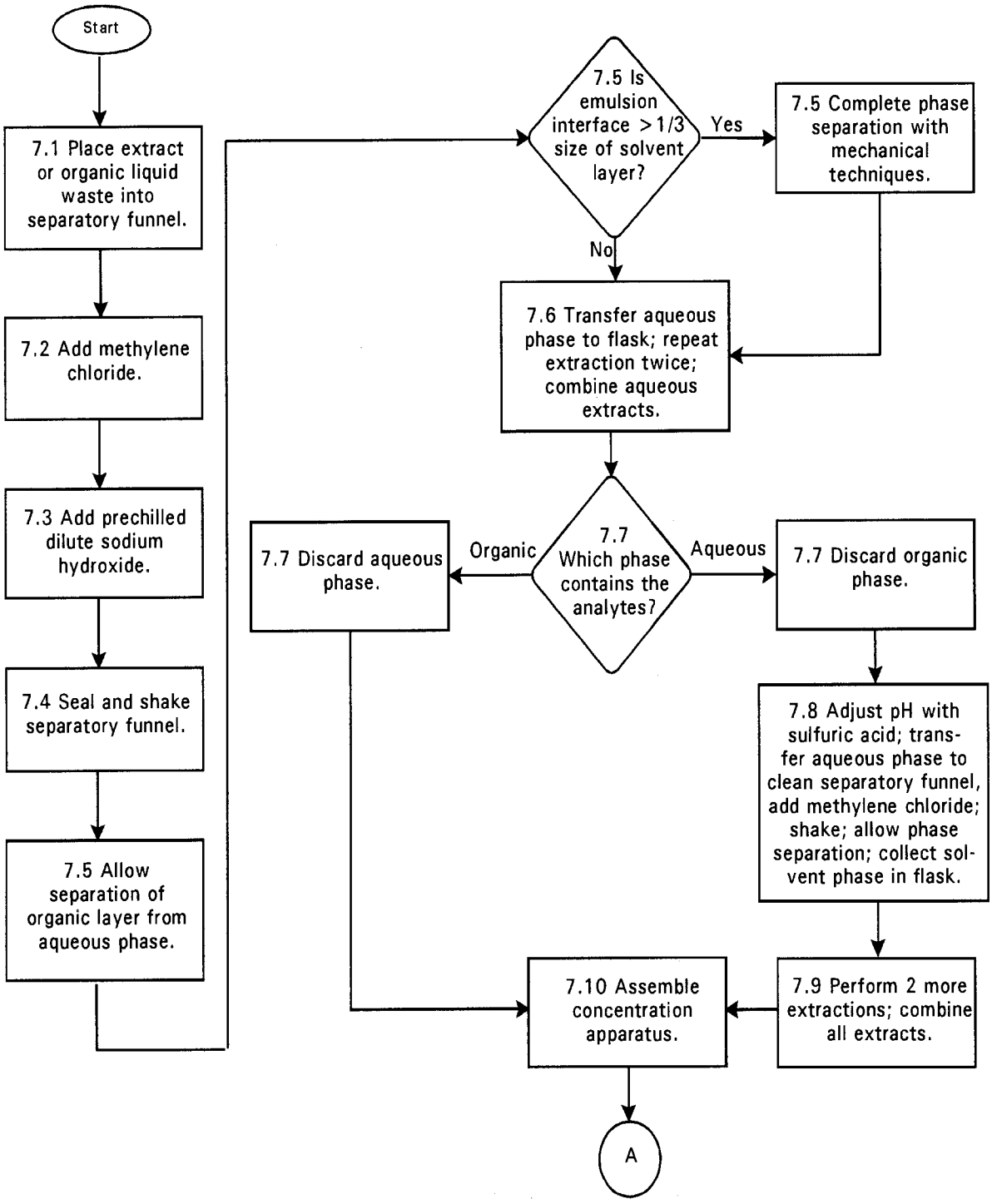
9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

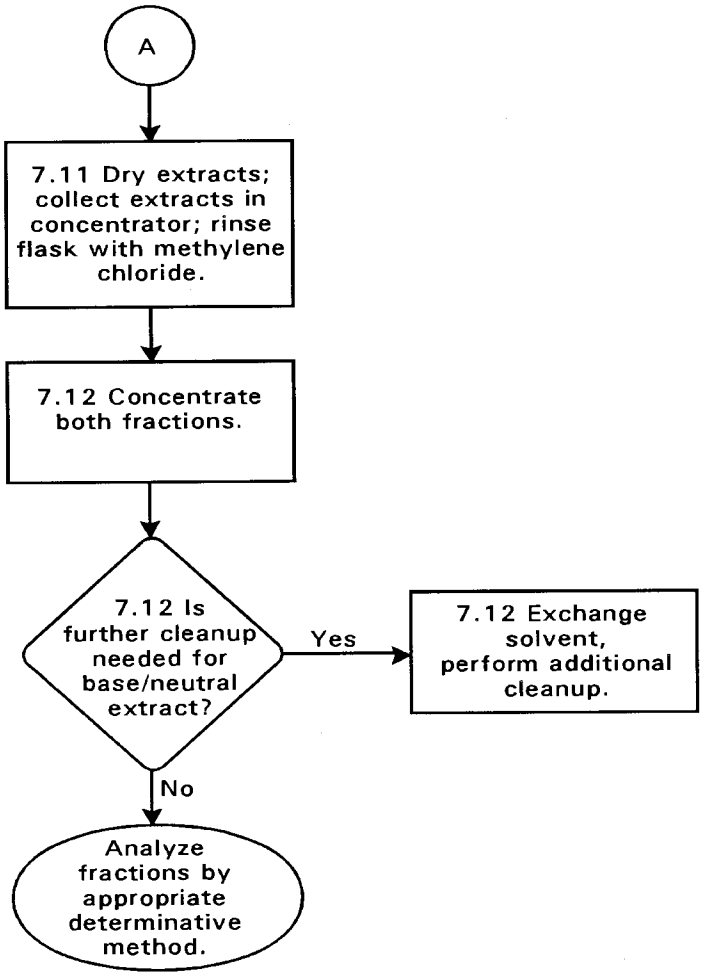
10.0 REFERENCES

1. Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1982; EPA-600/4-82-057.

ACID-BASE PARTITION CLEANUP



ACID-BASE PARTITION CLEANUP (Continued)



METHOD 3660B

SULFUR CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Elemental sulfur is encountered in many sediment samples (generally specific to different areas in the country), marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphorus pesticides. Therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. In general, sulfur will usually elute entirely in Fraction 1 of the Florisil cleanup (Method 3620).

1.2 Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors, flame photometric detectors operated in the sulfur or phosphorous mode, and Coulson electrolytic conductivity detectors in the sulfur mode. If the gas chromatograph is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through Aldrin.

1.3 Two techniques for the elimination of sulfur are detailed within this method: (1) the use of copper powder; and (2) the use of tetrabutylammonium sulfite. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organic compounds, while copper may degrade organophosphorus and some organochlorine pesticides.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The sample to undergo cleanup is mixed with either copper or tetrabutylammonium (TBA) sulfite. The mixture is shaken and the extract is removed from the sulfur cleanup reagent.

3.0 INTERFERENCES

The copper technique requires that the copper powder be very reactive, as evidenced by a bright shiny appearance (see Sec. 5.5 for the preparation of this reagent). However, care must be taken to remove all traces of the acid used to prepare the copper, in order to avoid degradation of some analytes.

4.0 APPARATUS AND MATERIALS

4.1 Mechanical shaker or mixer - Vortex Genie or equivalent.

4.2 Pipets, disposable - Pasteur type.

4.3 Centrifuge tubes, calibrated - 12 mL.

4.4 Glass bottles or vials - 10 mL and 50 mL, with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Nitric acid, HNO_3, dilute.

5.4 Solvents

5.4.1 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.4.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.4.3 2-Propanol, $CH_3CH(OH)CH_3$ - Pesticide quality or equivalent.

5.5 Copper powder - Remove oxides by treating with dilute nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone and dry under a stream of nitrogen. (Copper, fine granular Mallinckrodt 4649 or equivalent).

5.6 Tetrabutylammonium (TBA) sulfite reagent

5.6.1 Tetrabutylammonium hydrogen sulfate, $[CH_3(CH_2)_3]_4NHSO_4$.

5.6.2 Sodium sulfite, Na_2SO_3.

5.6.3 Prepare reagent by dissolving 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. To remove impurities, extract this solution three times with 20 mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a PTFE-lined screw cap. This solution can be stored at room temperature for at least one month.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Removal of sulfur using copper.

7.1.1 Concentrate the sample to exactly 1.0 mL or other known volume. Perform concentration using the techniques described in the appropriate 3500 series method.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.1.2 If the sulfur concentration is such that crystallization occurs, centrifuge to settle the crystals, and carefully draw off the sample extract with a disposable pipet leaving the excess sulfur in the concentration vessel. Transfer 1.0 mL of the extract to a calibrated centrifuge tube.

7.1.3 Add approximately 2 g of cleaned copper powder to the centrifuge tube. (The copper will fill the tube to approximately the 0.5 mL mark). Vigorously mix the extract and the copper powder for at least 1 min on the mechanical shaker. Allow the phases to separate.

7.1.4 Separate the extract from the copper by drawing off the extract with a disposable pipet and transfer to a clean vial. The volume remaining still represents 1.0 mL of extract.

NOTE: This separation is necessary to prevent further degradation of the pesticides.

7.2 Removal of sulfur using TBA sulfite

7.2.1 Concentrate the sample extract to exactly 1.0 mL or other known volume. Perform concentration using the techniques described in the appropriate 3500 series method.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.2.2 Transfer 1.0 mL of the extract to a 50 mL clear glass bottle or vial with a PTFE-lined screw-cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50 mL bottle.

7.2.3 Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 0.100 g portions until a solid residue remains after repeated shaking.

7.2.4 Add 5 mL organic free reagent water and shake for at least 1 min. Allow the sample to stand for 5-10 min. Transfer the hexane layer (top) to a concentrator tube and concentrate the extract to approximately 1.0 mL using the techniques described in the appropriate 3500 series method. Record the actual volume of the final extract.

7.3 Analyze the cleaned up extracts by gas chromatography (see the determinative methods, Sec. 4.3 of this chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 All reagents should be checked prior to use to verify that interferences do not exist.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the effect of using copper to remove sulfur on the recovery of certain pesticides.

10.0 REFERENCES

1. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9 (1971).

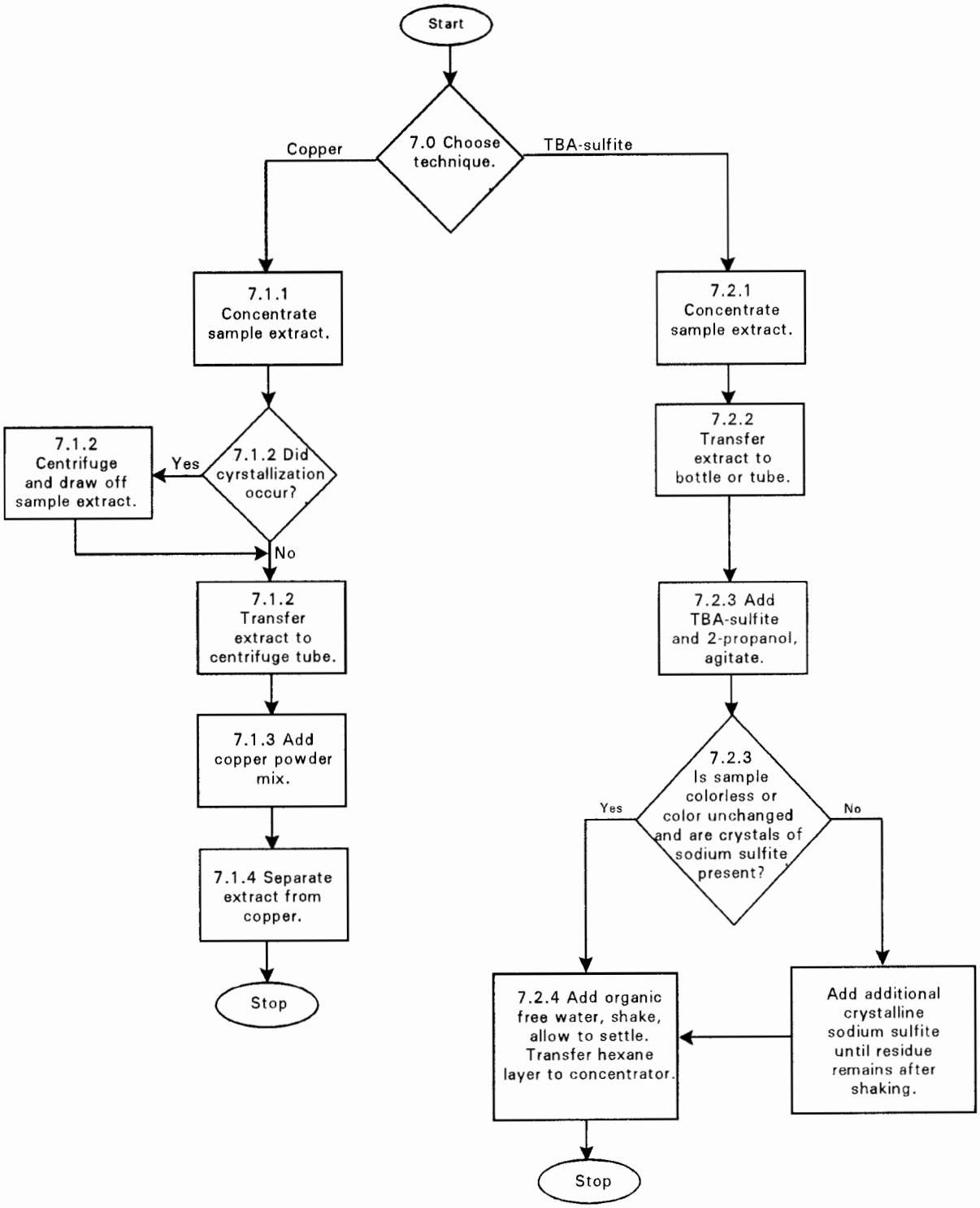
2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

TABLE 1
EFFECT OF COPPER ON PESTICIDES

Pesticide	Percent Recovery[a] Using Copper
Aroclor 1254	104.26
Lindane	94.83
Heptachlor	5.39
Aldrin	93.29
Heptachlor epoxide	96.55
DDE	102.91
DDT	85.10
BHC	98.08
Dieldrin	94.90
Endrin	89.26
Chlorobenzilate	0.00
Malathion	0.00
Diazinon	0.00
Parathion	0.00
Ethion	0.00
Trithion	0.00

a Percent recoveries cited are averages based on duplicate analyses for all compounds other than for Aldrin and BHC. For Aldrin, four and three determinations were averaged to obtain the result for copper. Recovery of BHC using copper is based on one analysis.

SULFUR CLEANUP



METHOD 3665A

SULFURIC ACID/PERMANGANATE CLEANUP

1.0 SCOPE AND APPLICATION

1.1 This method is suitable for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls. This method should be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

1.2 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 An extract is solvent exchanged to hexane, then the hexane is sequentially treated with (1) concentrated sulfuric acid and, if necessary, (2) 5% aqueous potassium permanganate. Appropriate caution must be taken with these corrosive reagents.

2.2 Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.

2.3 It is important that all the extracts be exchanged to hexane before initiating the following treatments.

3.0 INTERFERENCES

3.1 This technique will not destroy chlorinated benzenes, chlorinated naphthalenes (Halowaxes), and a number of chlorinated pesticides.

4.0 APPARATUS

4.1 Syringe or Class A volumetric pipet, glass; 1.0, 2.0 and 5.0 mL.

4.2 Vials - 1, 2 and 10 mL, glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

4.3 Vortex mixer.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades

may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid/Water, H_2SO_4/H_2O (1:1, v/v).

5.4 Hexane, C_6H_{14} - Pesticide grade or equivalent.

5.5 Potassium permanganate, $KMnO_4$, 5 percent aqueous solution (w/v).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sulfuric acid cleanup

7.1.1 Using a syringe or a volumetric pipet, transfer 1.0 or 2.0 mL of the hexane extract to a 10 mL vial and, in a fume hood, carefully add 5 mL of the 1:1 sulfuric acid/water solution.

7.1.2 The volume of hexane extract used depends on the requirements of the GC autosampler used by the laboratory. If the autosampler functions reliably with 1 mL of sample volume, 1.0 mL of extract should be used. If the autosampler requires more than 1 mL of sample volume, 2.0 mL of extract should be used.

CAUTION: Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

7.1.3 Cap the vial tightly and vortex for one minute. A vortex must be visible in the vial.

CAUTION: Stop the vortexing immediately if the vial leaks. AVOID SKIN CONTACT, SULFURIC ACID BURNS.

7.1.4 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer; it should not be highly colored nor should it have a visible emulsion or cloudiness.

7.1.5 If a clean phase separation is achieved, proceed to Sec. 7.1.8.

7.1.6 If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial and dispose of it properly. Add another 5-mL portion of the clean 1:1 sulfuric acid/water solution and perform another acid cleanup, beginning at Sec. 7.1.7

NOTE: Do not remove any hexane from the vial at this stage of the procedure.

If the extract is no longer colored, the analyst may either proceed with the permanganate cleanup (Sec. 7.2) or proceed with the final preparation (Sec. 7.3).

7.1.7 Vortex the sample for one minute and allow the phases to separate.

7.1.8 Transfer the hexane layer to a clean 10-mL vial. Take care not to include any of the acid layer in this clean vial, as it can cause damage to the analytical instrumentation. Once the hexane layer is removed, perform a second "extraction" of the acid layer, as described in Sec. 7.1.9.

7.1.9 Add an additional 1 mL of hexane to the sulfuric acid layer, cap and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

7.1.10 Remove the second hexane layer and combine with the hexane from Sec. 7.1.8.

7.2 Permanganate cleanup

The permanganate cleanup should be employed when the sulfuric acid cleanup has not removed all of the color from an extract.

7.2.1 Add 5 mL of the 5 percent aqueous potassium permanganate solution to the combined hexane fractions from 7.1.10.

CAUTION: Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

7.2.2 Cap the vial tightly and vortex for 1 minute. A vortex must be visible in the vial.

CAUTION: Stop the vortexing immediately if the vial leaks. AVOID SKIN CONTACT, POTASSIUM PERMANGANATE BURNS.

7.2.3 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer, it should not be highly colored nor should it have a visible emulsion or cloudiness.

7.2.4 If a clean phase separation is achieved, proceed to Sec. 7.2.7.

7.2.5 If the hexane layer is colored or the emulsion persists for several minutes, remove the permanganate solution from the vial via a glass pipette and dispose of it properly. Add another 5 mL of the clean aqueous permanganate solution.

NOTE: Do not remove any hexane at this stage of the procedure.

7.2.6 Vortex the sample and allow the phases to separate.

7.2.7 Transfer the hexane layer to a clean 10 mL vial.

7.2.8 Add an additional 1 mL of hexane to the permanganate layer, cap the vial securely and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

7.2.9 Remove the second hexane layer and combine with the hexane from Sec. 7.2.7.

7.3 Final preparation

7.3.1 Reduce the volume of the combined hexane layers to the original volume (1 or 2 mL) using an appropriate concentration technique, refer to the 3500 series methods.

7.3.2 Remove any remaining organochlorine pesticides from the extracts using Florisil Cleanup (Method 3620) or Silica Gel Cleanup (Method 3630).

7.3.3 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Sec. 4.3 of this chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a PTFE-lined screw cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

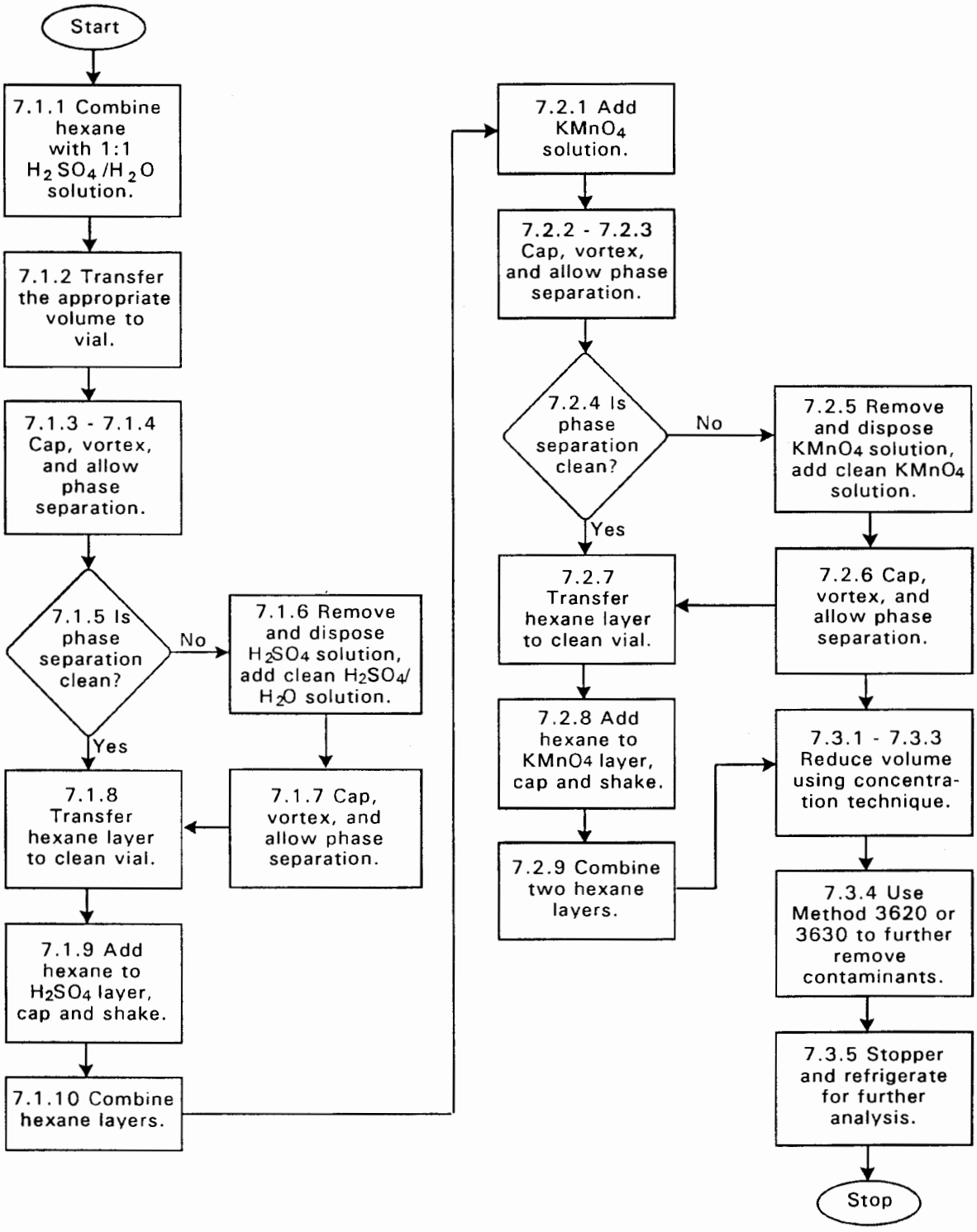
9.0 METHOD PERFORMANCE

9.1 No performance data are currently available.

10.0 REFERENCES

None required.

SULFURIC ACID/PERMANGANATE CLEANUP



METHOD 3810

HEADSPACE

1.0 SCOPE AND APPLICATION

1.1 Method 3810 was formerly Method 5020 in the second edition of this manual.

1.2 Method 3810 is a static headspace technique for extracting volatile organic compounds from samples. It is a simple method that allows large numbers of samples to be screened in a relatively short period of time. It is ideal for screening samples prior to using the purge-and-trap method. Detection limits for this method may vary widely among samples because of the large variability and complicated matrices of waste samples. The method works best for compounds with boiling points of less than 125°C. The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

1.3 Due to the variability of this method, this procedure is recommended for use only as a screening procedure for other, more accurate determinative methods (Methods 8010, 8015, 8020, 8030, and 8240).

2.0 SUMMARY OF METHOD

2.1 The sample is collected in sealed glass containers and allowed to equilibrate at 90°C. A sample of the headspace gas is withdrawn with a gas-tight syringe for screening analysis using the conditions specified in one of the GC or GC/MS determinative methods (8010, 8015, 8020, 8030, or 8240).

3.0 INTERFERENCES

3.1 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water. It may be necessary to wash out the syringe with detergent, rinse with distilled water, and dry in a 105°C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific determinative method for appropriate apparatus and materials.

4.2 Vials: 125-mL Hypo-Vials (Pierce Chemical Co., #12995, or equivalent), four each.

4.3 Septa: Tuf-Bond (Pierce #12720 or equivalent).

4.4 Seals: Aluminum (Pierce #13214l or equivalent).

4.5 Crimper: Hand (Pierce #13212 or equivalent).

4.6 Syringe: 5-mL, gas-tight with shutoff valve and chromatographic needles.

4.7 Microsyringe: 250- or 500-uL.

4.8 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

5.0 REAGENTS

5.1 Refer to the specific determinative method and Method 8000 for preparation of calibration standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Gas chromatographic conditions and Calibration: Refer to the specific determinative method for GC operating conditions and to Method 8000, Section 7.4, for calibration procedures.

7.2 Sample preparation:

7.2.1 Place 10.0 g of a well-mixed waste sample into each of two separate 125-mL septum-seal vials.

7.2.2 Dose one sample vial through the septum with 200 uL of a 50 ng/uL calibration standard containing the compounds of interest. Label this "1-ppm spike."

7.2.3 Dose a separate (empty) 125-mL septum seal vial with 200 uL of the same 50 ng/uL calibration standard. Label this "1-ppm standard."

7.2.4 Place the sample, 1-ppm-spike, and 1-ppm-standard vials into a 90°C water bath for 1 hr. Store the remaining sample vial at 4.0°C for possible future analysis.

7.3 Sample analysis:

7.3.1 While maintaining the vials at 90°C, withdraw 2 mL of the headspace gas with a gas-tight syringe and analyze by direct injection into a GC. The GC should be operated using the same GC conditions listed in the method being screened (8010, 8015, 8020, 8030, or 8240).

7.3.2 Analyze the 1-ppm standard and adjust instrument sensitivity to give a minimum response of at least 2 times the background. Record retention times (RT) and peak areas of compounds of interest.

7.3.3 Analyze the 1-ppm spiked sample in the same manner. Record RTs and peak areas.

7.3.4 Analyze the undosed sample as in Paragraph 7.3.3.

7.3.5 Use the results obtained to determine if the sample requires dilution or methanolic extraction as indicated in Method 5030.

8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 ug/g of sample, then the sensitivity of the instrument should be increased.

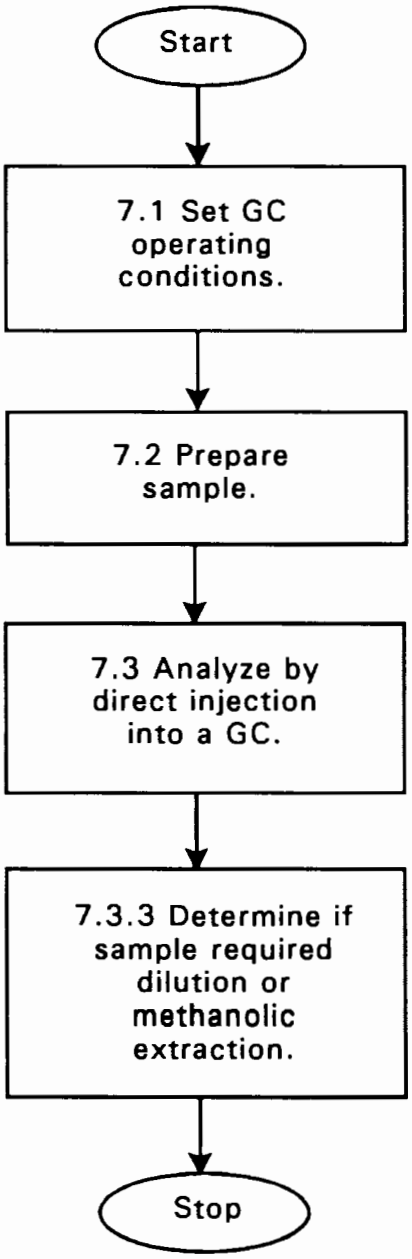
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Hachenberg, H. and A. Schmidt, Gas Chromatographic Headspace Analysis, Philadelphia: Hayden & Sons Inc., 1979.

2. Friant, S.L. and I.H. Suffet, "Interactive Effects of Temperature, Salt Concentration and pH on Headspace Analysis for Isolating Volatile Trace Organics in Aqueous Environmental Samples," Anal. Chem. 51, 2167-2172, 1979.


Start
7.1 Set GC operating conditions.
7.2 Prepare sample.
7.3 Analyze by direct injection into a GC.
7.3.3 Determine if sample required dilution or methanolic extraction.
Stop

METHOD 3820

HEXADECANE EXTRACTION AND SCREENING OF PURGEABLE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 This method is a screening procedure for use with purge-and-trap GC or GC/MS. The results of this analysis are purely qualitative and should not be used as an alternative to more detailed and accurate quantitation methods.

2.0 SUMMARY OF METHOD

2.1 An aliquot of sample is extracted with hexadecane and then analyzed by GC/FID. The results of this analysis will indicate whether the sample requires dilution or methanolic extraction prior to purge-and-trap GC or GC/MS analysis.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware. All these materials must be routinely demonstrated to be free from contaminants by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from sample to sample depending upon the nature and diversity of the water being sampled.

3.2 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 20x less sensitive than aromatics and haloethanes approximately 10x less sensitive. Low-molecular-weight, water-soluble solvents (e.g., alcohols and ketones) will not extract from the water, and therefore will not be detected by GC/FID.

4.0 APPARATUS AND MATERIALS

4.1 Balance: Analytical, capable of accurately weighing 0.0001 gm.

4.2 Gas Chromatograph: An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder (or equivalent). A data system is recommended for measuring peak heights and/or peak areas.

4.2.1 **Detector:** Flame ionization (FID).

4.2.2 **GC column:** 3-m x 2-mm I.D. glass column packed with 10% OV-101 on 100/120 mesh Chromosorb W-HP (or equivalent). The column temperature should be programmed from 80°C to 280°C at 16°C/min and held at 280°C for 10 min.

4.3 Centrifuge: Capable of accommodating 50-mL glass tubes.

4.4 Vials and caps: 2-mL for GC autosampler.

4.5 Volumetric flasks: 10- and 50-mL with ground-glass stopper or Teflon-lined screw-cap.

4.6 Centrifuge tubes: 50-mL with ground-glass stopper or Teflon-lined screw-cap.

4.7 Pasteur pipets: Disposable.

4.8 Bottles: Teflon-sealed screw-cap.

5.0 REAGENTS

5.1 Hexadecane and methanol: Pesticide quality or equivalent.

5.2 Reagent water: Reagent water is defined as water in which an interference is not observed at the method detection limit of each parameter of interest.

5.3 Stock standard solutions (1.00 ug/uL): Stock standard solutions can be purchased as certified solutions or can be prepared from pure standard materials.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in methanol in a 10-mL volumetric flask and dilute to volume (larger volumes may be used at the convenience of the analyst). If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially available stock standards may be used if they are certified by the manufacturer.

5.3.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. These standards should be checked frequently for signs of degradation or evaporation.

5.4 Standard mixture #1: Standard mixture #1 should contain benzene, toluene, ethyl benzene, and xylene. Prepare a stock solution containing these compounds as described in Paragraph 5.3 and then prepare a working standard (through dilution) in which the concentration of each compound in the standard is 100 ng/uL in methanol.

5.5 Standard mixture #2: Standard mixture #2 should contain n-nonane and n-dodecane. Prepare a stock solution containing these compounds as described in Paragraph 5.3. Dilute the stock standard with methanol so that the concentration of each compound is 100 ng/uL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 Water:

7.1.1.1 Allow the contents of the 40-mL sample vial to come to room temperature. Quickly transfer the contents of the 40-mL vial to a 50-mL volumetric flask. Immediately add 2.0 mL of hexadecane, cap the flask, and shake the contents vigorously for 1 min. Let phases separate. Open the flask and add sufficient reagent water to bring the hexadecane layer into the neck of the flask.

7.1.1.2 Transfer approximately 1 mL of the hexadecane layer to a 2.0-mL GC vial. If an emulsion is present after shaking the sample, break it by:

1. pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or

2. transferring the emulsion to a centrifuge tube and centrifuging for several min.

7.1.2 Standards:

7.1.2.1 Add 200 uL of the working standard mixtures #1 and #2 to separate 40-mL portions of reagent water. Follow the instructions in Sections 7.1.1.1 and 7.1.1.2 with the immediate addition of 2.0 mL of hexadecane.

7.1.3 Sediment/Soil:

7.1.3.1 Add approximately 10 g of sample (wet weight) to 40 mL of reagent water in a 50-mL centrifuge tube. Cap and shake vigorously for 1 min. Centrifuge the sample briefly. Quickly transfer the supernatant water to a 50-mL volumetric flask.

7.1.3.2 Follow the instructions given in Sections 7.1.1.1 and 7.1.1.2, starting with the addition of 2.0 mL of hexadecane.

7.2 Analysis:

7.2.1 **Calibration:**

7.2.1.1 External standard calibration: The GC/FID must be calibrated each 12-hour shift for half of full-scale response when

injecting 1-5 uL of each extracted standard mixture #1 and #2 (Paragraphs 5.4 and 5.5).

7.2.2 **GC/FID analysis:** Inject the same volume of hexadecane extract for the sample under investigation as was used to perform the external standard calibration. The GC conditions used for the standards analysis must also be the same as those used to analyze the samples.

7.2.3 **Interpretation of the GC/FID chromatograms:** There are two options for interpretation of the GC/FID results.

7.2.3.1 Option A: The standard mixture #1 is used to calculate an approximate concentration of the aromatics in the sample. Use this information to determine the proper dilution for purge-and-trap if the sample is a water. If the sample is a sediment/soil, use this information to determine which GC/MS purge-and-trap method (low- or high-level) should be used. If aromatics are absent from the sample or obscured by higher concentrations of other purgeables, use Option B.

7.2.3.2 Option B: The response of standard mixture #2 is used to determine which purge-and-trap method should be used for analyzing a sample. All purgeables of interest have retention times less than the n-dodecane retention time. A dilution factor (Paragraph 7.2.4.1.3) may be calculated for water samples, and an X factor (Paragraph 7.2.4.2.3) for soil/sediment samples, to determine whether the low- or high-level purge-and-trap procedure should be used.

7.2.4 Analytical decision point:

7.2.4.1 Water samples: Compare the hexadecane sample extract chromatograms against an extracted standard chromatogram.

7.2.4.1.1 If no peaks are noted, analyze a 5-mL water sample by the purge-and-trap method.

7.2.4.1.2 If peaks are present prior to the n-dodecane peak and aromatics are distinguishable, follow Option A (Paragraph 7.2.3.1).

7.2.4.1.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, Option B should be used as follows: If all peaks (prior to n-dodecane) are <3% of the n-nonane, analyze 5 mL of water sample by the purge-and-trap method. If any peak is >3% of the n-nonane, measure the area of the major peak and calculate the necessary dilution factor as follows:

$$\text{dilution factor} = 50 \times \frac{\text{area of major peak in sample}}{\text{peak area of n-nonane}}$$

The water sample should be diluted using the calculated factor just prior to purge-and-trap GC or GC/MS analysis.

7.2.4.2 **Soil/sediment samples:** Compare the hexadecane sample extract chromatograms against an extracted standard chromatogram.

7.2.4.2.1 If no peaks are noted, analyze a 5-g sample by the low-level purge-and-trap procedure.

7.2.4.2.2 If peaks are present prior to the n-dodecane and aromatics are distinguishable, follow Option A using the concentration information given in Table 1 to determine whether to analyze the sample by a low- or high-level purge-and-trap technique.

7.2.4.2.3 If peaks are present prior to n-dodecane but aromatics are absent or indistinguishable, use Option B. Calculate an X factor for the sample using the following equation:

$$X \text{ factor} = \frac{\text{area of major peak in sample}}{\text{area of n-nonane}}$$

Use the information provided in Table 1 to determine how the sample should be handled for GC/MS analysis.

7.2.4.2.4 If a high-level method is indicated, the information provided in Table 2 can be used to determine the volume of methanol extract to add to 5 mL of reagent water for analysis (see Methods 5030 and 8240 for methanolic extraction procedure).

8.0 QUALITY CONTROL

8.1 It is recommended that a reagent blank be analyzed by this screening procedure to ensure that no laboratory contamination exists. A blank should be performed for each set of samples undergoing extraction and screening.

9.0 METHOD PERFORMANCE

9.1 No data available.

10.0 REFERENCES

1. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

TABLE 1. DETERMINATION OF GC/MS PURGE-AND-TRAP METHOD

X Factor	Approximate Concentration Range [a]	Analyze by
0-1.0	0-1,000 ug/kg	Low-level method
>1.0	>1,000 ug/kg	High-level method

[a] This concentration range is based upon the response of aromatics to GC/FID. The concentration for halomethanes is 20x higher, and haloethanes 10x higher, when comparing GC/FID responses.

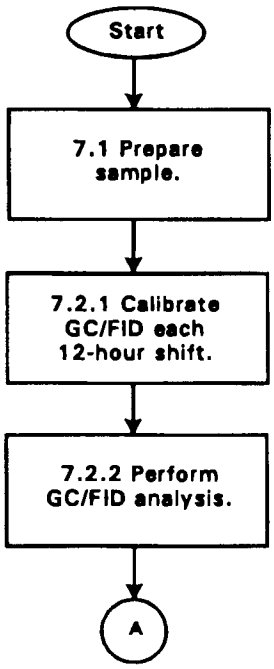
TABLE 2. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-LEVEL SOIL/SEDIMENTS

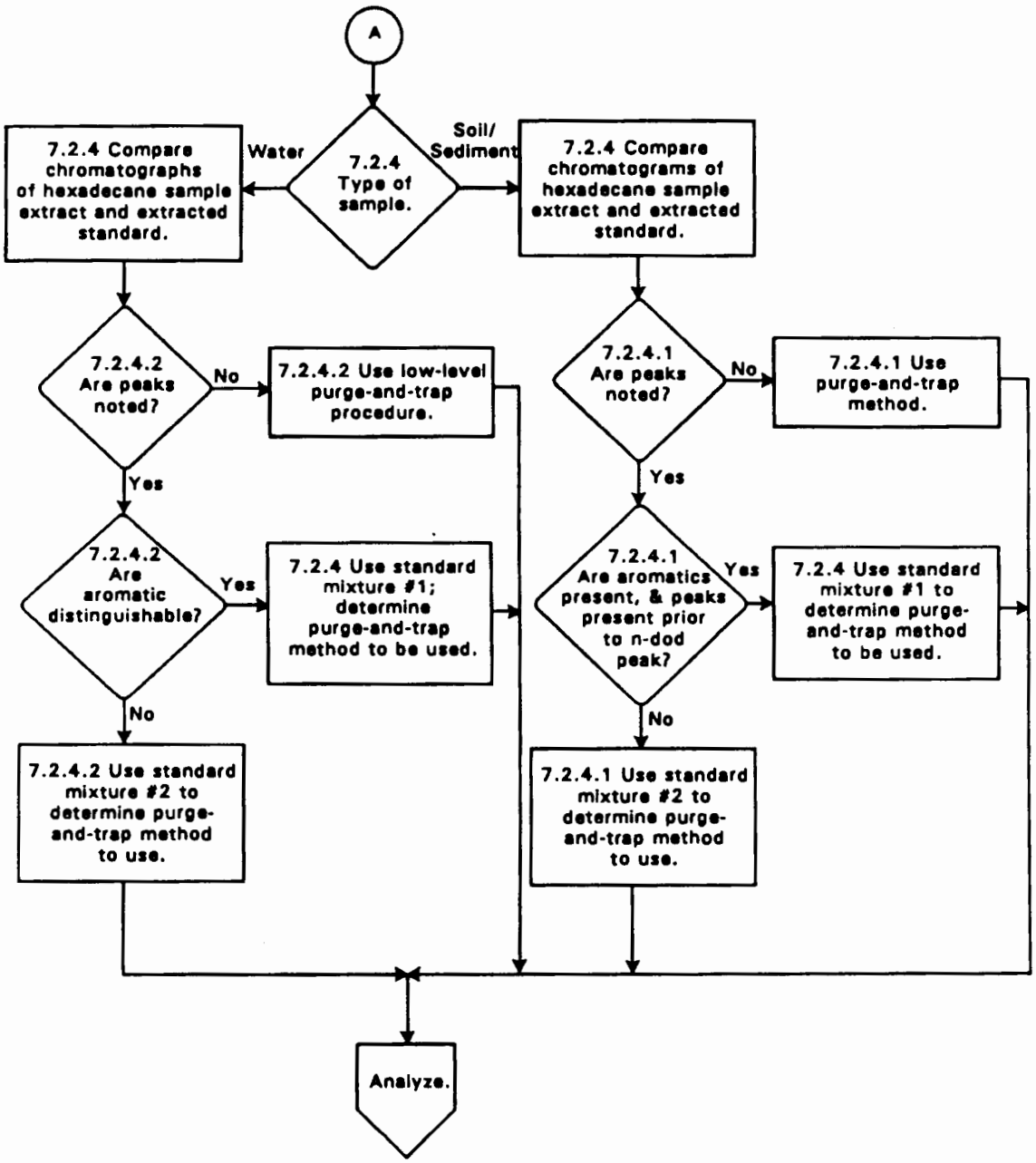
X Factor	Approximate Concentration Range [a]	Volume of Methanol Extract [b]
0.25-5.0	500-10,000 ug/kg	100 ul
0.5-10.0	1,000-20,000 ug/kg	50 ul
2.5-50.0	5,000-100,000 ug/kg	10 ul
12.5-250	25,000-500,000 ug/kg	100 uL of 1/50 dilution [c]

[a] Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

[b] The volume of methanol added to 5 mL of water being purged should be 100 uL. Therefore if the amount of methanol extract required is less than 100 uL, additional methanol should be added to maintain the constant 100-uL volume.

[c] Dilute an aliquot of the methanol extract and then take 100 uL for analysis.


Start
7.1 Prepare sample.
7.2.1 Calibrate GC/FID each 12-hour shift.
7.2.2 Perform GC/FID analysis.
A


A
7.2.4 Type of sample.
Water
Soil/ Sediment
7.2.4 Compare chromatographs of hexadecane sample extract and extracted standard.
7.2.4 Compare chromatograms of hexadecane sample extract and extracted standard.
7.2.4.2 Are peaks noted?
No
7.2.4.2 Use low-level purge-and-trap procedure.
Yes
7.2.4.2 Are aromatic distinguishable?
Yes
7.2.4 Use standard mixture #1; determine purge-and-trap method to be used.
No
7.2.4.2 Use standard mixture #2 to determine purge-and-trap method to use.
7.2.4.1 Are peaks noted?
No
7.2.4.1 Use purge-and-trap method.
Yes
7.2.4.1 Are aromatics present, & peaks present prior to n-dod peak?
Yes
7.2.4 Use standard mixture #1 to determine purge-and-trap method to be used.
No
7.2.4.1 Use standard mixture #2 to determine purge-and-trap method to use.
Analyze.

METHOD 4000

IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Immunoassay is an analytical technique useful for the separation, detection and quantitation of both organic and inorganic analytes in diverse environmental and waste matrices. Immunoassay methods are used to produce two types of quantitative results: 1) range-finding or screening results indicative of compliance with an action level, and 2) assay values.

1.2 Commercially-available testing products present immunoassay protocols that are rapid, simple and portable. These products can be used effectively in both laboratory and field settings, and require limited training. These test products substantially increase the number of data points that can be generated within a given time period, and permit an operator to analyze a number of samples simultaneously, within a relatively short period of time. Results are available immediately upon completion of the test, and can assist in the on-site management of personnel and equipment, as well as the data management activities of the laboratory.

1.2.1 A list of validated immunoassay testing products is available from the USEPA Office of Solid Waste.

1.3 Section 11.0 provides a glossary of basic immunoassay terms.

1.3.1 The glossary is not intended to be comprehensive, but to provide basic definitions that will assist in understanding product inserts and publications relating to immunoassay technology.

1.3.2 The performance of test products will vary from manufacturer to manufacturer. The performance claims and limitations of each test product will be provided in the package insert. The package insert of each test product purchased should be read to determine if the performance is acceptable for a given application.

2.0 SUMMARY OF METHOD

2.1 The immunoassay test products available will often vary in both format and chemistry. The characteristics of a specific product are described in the package insert provided by the manufacturer. This summary is, therefore, general in scope, and is intended to provide a general description of the more common elements of these methods.

Immunoassay test products use an antibody molecule to detect and quantitate a substance in a test sample. These testing products combine the specific binding characteristics of an antibody molecule with a detection chemistry that produces a detectable response used for interpretation. In general, antibody molecules specific for the method's intended target are provided at a predefined concentration. A reporter (i.e., signal generating) reagent, composed of the target compound conjugated to a signal producing compound or molecule (e.g., enzymes, chromophores, fluorophores, luminescent compounds, etc.), is also provided. The concentration, affinity, and specificity of the products' antibody influences performance, as does the chemistry of the reporter reagent.

The reporter reagent and antibody molecules of a given product are binding partners, and complex in solution. The addition of a positive sample containing the target substance to this solution results in a competitive binding reaction between the target analyte and the reporter reagent for the antibody sites. The antibody concentration, and therefore binding capacity, is limited to prevent the simultaneous binding of both the reporter and target molecules. The concentration of reporter reagent that can bind to the antibody is inversely proportional to the concentration of substance in the test sample.

Immunoassay methods may be heterogeneous (i.e., requiring a wash or separation step), or homogeneous (i.e., not requiring a separation step). In commonly available heterogeneous testing products, the antibody is immobilized to a solid support such as a disposable test tube, and the bound reporter reagent will be retained after removing the unbound contents of the tube by washing. Therefore, a negative sample results in the retention of more reporter molecules than a positive sample. The analysis of a standard containing a known concentration results in the immobilization of a proportional concentration of reporter reagent. A positive sample (i.e., containing a higher concentration than the standard) results in the immobilization of fewer reporter molecules than the standard, and a negative sample (i.e., containing less than the standard) will immobilize more.

2.2 A chemistry of the detection of the immobilized reporter is used for interpretation of results. The reporter molecule may be a conjugate of the target molecule and a directly detectable chromophore, fluorophore, or other specie, or conjugated to an enzyme that will act upon a substrate to produce the detectable response. Immunoassay testing products have a quantitative basis, and will produce a signal that is dependant on the concentration of analyte present in the sample. For environmental immunoassay methods, the signal produced is exponentially related to the concentration of the compounds present. Many immunoassay methods use enzymes to develop chromogenic response, and are termed enzyme immunoassays. Assays that generate a chromogenic response are analyzed photometrically, and use the principles of Beer's Law (Absorbance = Extinction Coefficient x Concentration x Path Length) to determine the concentration of analyte in a sample.

Immunoassay methods can provide quantitative data when configured with a series of reference standards that are analyzed and used to construct a standard curve. The signal generated from the analysis of a test sample is used to determine concentration by interpolation from the standard curve. Alternatively, these testing products can be configured to determine if a sample is positive or negative relative to a single standard.

Individual immunoassay testing products are reviewed and accepted by the EPA-OSW for the detection of sample analytes in specified matrices. A variety of testing products, produced by several different developers, may be available for the same compound(s) and matrices. Each of theses methods have been formulated using independently developed reagents that may result in significantly different performance characteristics and limitations.

The performance of the immunoassay testing products ultimately relates to the characteristics of the antibody, reporter molecule, and sample processing chemistry. The dose-response characteristics of a method, the position of the standard relative to the claimed action level, and the stated cross-reactivity characteristics of the selected test product, provide relevant information regarding the performance and recognition profile of the selected test product.

The precision, and ultimately the sensitivity of an immunoassay method, is a function of the signal-to-noise characteristics of its dose-response curve, and its operational consistency. Methods having a high slope and low non-specific signal generation produce the most sensitive and precise methods. Signal imprecision applied to a dose-response curve having a shallow slope exhibits

proportionally greater imprecision in the calculated concentration than would a method having a steeper slope. In an action level testing product, this would cause the reference standard to be positioned further from the action level, increasing the incidence of false positive results. Similarly, a method having less non-specific signal generation (higher signal-to-noise ratio) will be more sensitive and precise when other characteristics (i.e., dose-response slope) are held constant.

Immunoassay methods are used to detect contamination at a specific concentration below the claimed detection level for the test product. For example, an immunoassay used to detect PCB contamination in soil at 1 ppm will include a standard preparation containing less than 1 ppm. The reference preparation concentration is positioned to minimize the incidence of false negative results at the claimed detection level. For remediation and monitoring applications, where action levels of interest are defined, immunoassay methods should exhibit a negligible incidence of false negative results, and minimal false positives.

For a single point action level test, the concentration of analyte relative to the action level is selected by the developer, and is influenced by the precision (i.e., intra-assay, inter-person, inter-lot, inter-day, etc.), sample matrix interferences and other performance characteristics and limitations of the basic method. The concentration of analyte in the reference materials should be less than, but close to, the claimed action level. The concentration selected for the standard defines the concentration that will produce a 50% incidence of false positive results by the test product. While this issue is one representing limited liability to the operator, it is a practical issue that often requires attention. An immunoassay method for the detection of 1 ppm of PCB using a standard containing 0.8 ppm of PCB will experience a 50% false positive incidence in samples containing 0.8 ppm of PCB, and some incidence of false positive results in a sample containing between 0.8 and 1 ppm. A similar immunoassay that uses a standard containing 0.4 ppm will experience a 50% false positive incidence in samples containing 0.4 ppm of PCB, and some incidence of false positive results in a sample containing between 0.4 and 1 ppm. The closer the standard concentration is to the action level, the better the overall performance.

2.3 Cross reactivity characteristics illustrate the specificity of the underlying immunochemistry. The antibody molecules used by a test product bind to a target compound and then participate in the process of generating the signal used for interpretation. Antibody molecules bind by conformational complimentarity. These molecules can be exquisitely specific, and can differentiate subtle differences in the structure of a compound. The binding characteristics of reagents in different test products can vary, and influence the recognition profile and incidence of false results obtained by the method. Immunoassay methods should detect the target analytes claimed by the test product and exhibit limited recognition for compounds and substances not specified.

3.0 INTERFERENCES

3.1 Non-target analytes may bind with the antibody present, producing a false-positive result. These non-target analytes may be similar to the target analytes, or they may be chemically dissimilar co-contaminants. During evaluation of each test product for RCRA testing applications, studies were conducted to determine these "cross-reactive" constituents. At a minimum, these studies evaluated the response of the test product to all other similar RCRA analytes in that analyte class, as well as for selected lists of non-RCRA analytes. This testing scheme is designed to ensure that all other similar RCRA analytes and likely co-contaminants are evaluated during cross-reactivity testing. The results of these studies are presented in each method in tabular form, providing separate data sets for each test product evaluated.

3.2 Interference in the binding of an antibody to its target compound, or reporter molecule reagent, may occur when testing sample matrices with confounding contaminants or circumstances (e.g., oil, pH, temperature, some solvents). Immunoassay products contain sample processing technology that has been developed and validated for use with specified matrices. Interferences incurred from the testing of incompatible matrices may prevent the testing product from meeting its performance claims, and increase the number of false positive or false negative results. Individual immunoassay products designate the intended sample matrices.

3.3 Immunoassay products differ in shelf-life and storage requirements. Test products that are operated outside of the shelf-life and storage temperature recommendations may not provide the claimed performance.

3.4 Some test products have designated temperature ranges for operation. When these products are used, all tests must be performed within the specified operating temperature limits, or else false negative/positive results may exceed performance claims.

4.0 APPARATUS AND MATERIALS

4.1 Each test product will specify the apparatus and materials provided, as well as any additional apparatus and materials necessary for performance of the test.

5.0 REAGENTS

5.1 The two basic reagents used in immunoassay analysis are the antibody (e.g., anti-PCP) and reporter conjugate reagent (e.g., PCP molecules bound to an enzyme).

5.1.1 The formation of antibodies to haptenic molecules (i.e., most environmental contaminants) is induced by the derivatization and coupling of molecules of the target analytes to large carrier molecules such as albumin, hemocyanin or thyroglobulin. The increased size and complexity of the immunogen (antigen) conjugate, once injected, is sufficient to stimulate the immune system to produce an antibody response. The effectiveness of the immunogen in producing antibodies having the prerequisite binding characteristics and recognition profile is influenced by the surface density of the chemical groups on the carrier molecule, the nature of the bridge chemistry used, the point of attachment, the immunization protocol, immunogen concentration, adjuvants (i.e., immune response stimulants), and the species of the host animal.

5.1.2 An enzyme-reporter conjugate reagent is synthesized by coupling a target analyte or derivative of a target analyte to an enzyme, such as horseradish peroxidase. Enzymes enhance the sensitivity of the method by action on a substrate and the production and catalytic amplification of the detection signal. A single enzyme molecule used in immunoassay methods will convert approximately 10^6 molecules of a target analyte into a detectable product within one minute at ambient temperature.

5.2 Each test product will specify the reagents provided, as well as any additional reagents necessary for performance of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Testing of solid waste by immunoassay requires production of a reproducible, particulate free leachate. It is critical that this leachate be produced using a solvent that allows the reproducible extraction and recovery of the target analytes, and is compatible with the antibody/enzyme conjugate of the immunoassay system used. Buffers, detergents, and solvents, used together or in combination, have been used effectively for extraction. Filtration of particulate matter may be integrated into the immunoassay test, or accomplished as a separate step within the protocol.

6.2 The immunoassay test products included in SW-846 methods will provide explicit waste- or medium-specific directions for handling samples and extraction of target analytes.

6.3 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 The specific procedure for each immunoassay test product is supplied by the manufacturer in the package insert.

7.2 The recognition characteristics, sensitivity, detection ranges(s), effective operating temperature, interferences and cross-reactivity of the test will depend on the product being used.

7.3 Immunoassay methods include both a sample processing and immunoassay component. It should be noted that the immunochemical reagents and sample processing components supplied with each product is specific to each manufacturer. Methods available from different manufacturers for the same compound and application may have significantly different performance characteristics.

8.0 QUALITY CONTROL

8.1 The performance of the tests cited in the immunoassay methods in this manual has been reviewed, and found to be consistent with the claims that are made in the manufacturer's literature. In order to meet this performance expectation, the analyst must:

- Follow the manufacturer's instructions for the test product being used,
- Use test products before the specified expiration date,
- Use reagents only with the test products for which they are designated,
- Use the test products within their specified storage temperature and operating temperature limits.

8.2 It is important to evaluate the performance claims and limitation provided with each testing product to determine its application to a specific matrix and testing program.

8.3 Refer to Chapter One for standard quality control procedures.

9.0 METHOD PERFORMANCE

9.1 A false negative is defined as a negative response for a sample containing the target analytes at or above the stated action level. False negative rate is measured by analyzing split

samples using both the test product and a separate reference method. False negative data are provided in each method for each test product evaluated.

9.2 A false positive is defined as a positive response for a sample that contains analytes below the specified action level. Like false negatives, false positive rates are measured by analyzing split samples with both the test product and a separate reference method. False positive data are provided in each method for each test product evaluated.

9.3 Cross-reactivity and recognition profile data are provided at the end of each method in tabular form, providing separate data sets for each test product evaluated. Using these data, the analyst can evaluate if contaminants are present which are likely to produce a false positive response, and the magnitude of that response.

9.4 For single-point tests, sensitivity data are provided demonstrating the concentration of target analyte(s) that can be detected with greater than 95% confidence.

9.5 Data are provided demonstrating the bias of the testing products accepted. These data may be from:

- serial dilution of samples (i.e., is the recovery of target analyte a function of concentration?),
- sample recovery studies, and
- studies correlating the results of the testing product with a reference method.

9.6 Data are provided demonstrating that the extraction efficiency of the test being evaluated correlates with that of the referenced method.

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11.0 GLOSSARY OF TERMS

Antigen	A molecule that induces the formation of an antibody.
Antibody	A binding protein which is produced in response to an antigen, and which has the ability to bond with the antigen that stimulated its production.
B Lymphocyte (B Cell)	A type of lymphocyte that, upon stimulation, differentiates into an antibody-secreting plasma cell.
% BO	A quantitative expression of the sensitivity of an immunoassay, calculated as $(OD_{sample}/OD_{blank})x100$
Carrier	An immunogenic substance that, when coupled to a hapten, renders the hapten immunogenic.
Competitive Immunoassay	An immunoassay method involving an *in-vitro* competitive binding reaction.
Cross-Reactivity	The relative concentration of an untargeted compound that would produce a response equivalent to a specified concentration of the targeted compound. In a semi-quantitative immunoassay, it provides an indication of the concentration of cross-reactant that would produce a positive response. Cross-reactivity for individual compounds is often calculated as the ratio of target analyte concentration to the cross-reacting compound concentration at 50% inhibition of the immunoassay's maximum signal X 100%.
Dose-Response Curve	Representation of the signal generated by an immunoassay (y axis) plotted against the concentration of the target compound (x axis) in a series of standards of known concentration. When plotting a competitive immunoassay in a rectilinear format, the dose-response will have a hyperbolic character. When the $\log_{10}$ of concentration is used, the plot assumes a sigmoidal shape, and when the log of signal is plotted against the logit transformation of concentration, a straight line plot is produced.
ELISA	*Enzyme Linked Immunosorbent Assay* is an enzyme immunoassay method that uses an immobilized reagent (*e.g.*,antibody adsorbed to a plastic tube), to facilitate the separation of targeted analytes (antibody-bound components) from non-target substances (free reaction components) using

	a washing step, and an enzyme conjugate to generate the signal used for the interpretation of results.
Enzyme Conjugate	A molecule produced by the coupling of an enzyme molecule to a targeted analyte that is responsible for acting upon a substrate to produce a detectable signal.
Enzyme Immunoassay	An immunoassay method that uses an enzyme conjugate reagent to generate the signal used for interpretation of results. The enzyme mediated response may take the form of a chromogenic, fluorogenic, chemiluminescent or potentiometric reaction. (*see Immunoassay and ELISA*)
False Negatives	A negative interpretation of the method containing the target analytes at or above the detection level. Ideally, an immunoassay test product included in an SW-846 method should produce no false negatives. The maximum permissible false negative rate is 5%, as measured by analyzing split samples using both the test product and a reference method.
False Positives	A positive interpretation for a sample is defined as a positive response for a sample that contains analytes below the action level.
Hapten	A substance that cannot directly induce an immune response (e.g., antibody production), but can bind to the products of an immune response (e.g., antibody) when that response is induced by an alternate mechanism. Chemical contaminants of the environment are haptens.
Hapten-Carrier Conjugate	The coupling of a non-immunogenic molecule (e.g., targeted analyte) to an immunogenic substance (e.g., bovine serum albumin, keyhole limpet hemocyanin) for the purpose of stimulating an immune response.
Heterogeneous Immunoassay Methods	Immunoassay methods that include steps for the separation of substances that become bound to the antibody from those that remain free in solution.
Homogeneous Immunoassay Methods	Immunoassay methods that do not require the separation of bound and free substances, but that utilize antibody molecules that can bind and directly modulate the signal produced by the reporter molecule (e.g., enzyme conjugate).
Immunoassay	An analytical technique that uses an antibody molecule as a binding agent in the detection and quantitation of substances in a sample. (*see Enzyme Immunoassay and ELISA*)
Immunogen	A substance having a minimum size and complexity, and that is sufficiently foreign to a genetically competent host to stimulate an immune response.

Ligand	The molecule, ion or group that forms a complex with another molecule.
Lymphocytes	One of the five classes of white blood cells found in the circulatory system of vertebrates. A mononuclear cell 7-12 µm in diameter containing a nucleus with densely packed chromatin and a small rim of cytoplasm.
Monoclonal Antibodies	Identical copies of antibody molecules that have a common set of binding characteristics.
Optical Density (OD)	Synonymous with *Absorbance*, Optical Density is the amount of light being absorbed at a given frequency, as given by the following equation: $OD = \log I_o - \log I$, where: I_o is the intensity of the incident light, I is the intensity of the transmitted light
Polyclonal Antibodies	A group of antibody molecules that differ in amino acid composition and sequence, and that exhibit binding characteristics. Polyclonal antibodies are produced from a simulation of multiple clones of lymphocytes.
Substrate	Reagents that produce detectable signal when acted upon by enzyme conjugate.

METHOD 4010A

SCREENING FOR PENTACHLOROPHENOL BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4010 is a procedure for screening solids such as soils, sludges, and aqueous media such as waste water and leachates for pentachlorophenol (PCP) (CAS Registry No. 87-86-5).

1.2 Method 4010 is recommended for screening samples to determine whether PCP is likely to be present at defined concentrations (i.e., kits are available which give positive results at 0.005 mg/L for aqueous samples, and at 0.5, 10 or 100 mg/kg in solid samples). Method 4010 provides an estimate for the concentration of PCP by comparison with a standard.

1.3 Using the test kits from which this method was developed, 95% of aqueous samples containing 2 ppb or less of PCP will produce a negative result in the 5 ppb configuration. Also, 95% of soil samples containing 125 ppb or less of PCP will produce a negative result in the 5000 ppb test configuration.

1.4 In cases where the exact concentration of PCP is required, additional techniques (i.e., gas chromatography (Methods 8141, 8151) or gas chromatography/mass spectrometry (Method 8270)) should be used.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed.

2.2 In general, the method is performed using a water sample or an extract of a water sample. The sample/extract and an enzyme conjugate reagent are added to immobilized antibody. The enzyme conjugate "competes" with PCP present in the sample for binding to immobilized anti-PCP antibody. The test is interpreted by comparing the response produced by testing a sample to the response produced by testing standard(s) simultaneously.

3.0 INTERFERENCES

3.1 Compounds that are chemically similar may cause a positive test (false positive) for PCP. The test kits used in preparation of this method were evaluated for interferences. Tables 1A and 1B provide the concentration of compounds which will give a false positive test at the indicated concentration.

3.2 Other compounds have been tested for cross reactivity for PCP and have been demonstrated not to interfere with the specific kits tested. Consult the information provided by the manufacturer of the kit used for additional information regarding cross reactivity with other compounds.

3.3 Storage and use temperatures may modify the method performance. Follow the manufacturer's directions for storage and use.

4.0 APPARATUS AND MATERIALS

Immunoassay test kit: PENTA RISc™ (EnSys, Inc.), EnviroGard™ PCP in Soil (Millipore, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Soil samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance specifications indicated in Tables 2-10.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Method 4000 and Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other test kits.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4010 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 This method has been applied to a series of groundwater, process water, and wastewater samples from industries which use PCP, and the results compared with GC/MS determination of PCP (Method 8270). These results are provided in Table 2. These results represent determinations by two laboratories using the PENTA RISc™ test kit.

9.2 This method has been applied to a series of soils from industries which use PCP and the results compared with GC/MS determination of PCP via method 8270. These results are provided in Table 3. These results represent determinations by two laboratories using the PENTA RISc™ test kit.

9.3 Sensitivity of the EnviroGard PCP in Soil Test Kit was determined by establishing the "noise" level expected from matrix effects encountered in negative soil samples and determining the corresponding PCP concentration by comparison to the analyte-specific response curve. Eight different soils which did not contain PCP were assayed. Each of these soils was extracted in triplicate and each extract was analyzed in three different assays. The mean and the standard deviation of the resulting %Bo's (%Bo = $[(OD_{sample}/OD_{negative\ control})x100]$, see definitions in Method 4000) were calculated and the sensitivity was estimated at two standard deviations below the mean. The sensitivity for Method 4010 was determined to be 80% Bo at a 95% confidence interval. Based on the average assay response to PCP, this corresponds to 2 ppm PCP. These data are shown in Table 4.

9.4 The effect of water content of the soil samples on the EnviroGard™ PCP in Soil test kit was determined by assaying three different soil samples which had been dried and subsequently had water added to 30% (w/w). Aliquots of these samples were then fortified with PCP. Each soil sample was assayed three times, with and without added water, and with and without home heating oil (HHO) fortification. It was determined that water in soil up to 30% had no detectable effect on the method. These data are shown in Table 5.

9.5 The effect of the pH of the soil extract on the EnviroGard™ PCP in Soil test kit was determined by adjusting the soil pH of three soil samples. Soil samples were adjusted to pH 2 - 4 using 6N HCl and pH 10 - 12 using 6N NaOH. Aliquots of the pH adjusted soil samples were fortified with PCP and the unfortified and fortified samples were extracted. These extracts were assayed three times. It was determined that soil samples with pH ranging from 3 to 11 had no detectable effect on the performance of the method. These data are shown in Table 6.

9.6 The bias of the EnviroGard™ PCP in Soil test kit was estimated by fortifying three different soil samples at two different concentrations (10 and 100 ppm PCP). Each fortified sample was extracted three times and each extract was assayed three times. Recovery for individual determinations ranged from 60% to 125%. Average recovery for each individual extract ranged from 72% to 101%. Overall average recovery for all samples was 86%. These data are summarized in Table 7.

9.7 The effect of co-contamination of soil samples with oil on the EnviroGard™ PCP in Soil test kit was investigated. Three soil samples were adulterated with diesel oil and aliquots were fortified with PCP. The samples were extracted and the extracts each assayed three times. It was determined that no interference was detected in samples with up to 10% oil contamination. The data from samples adulterated at 10% are shown in Table 8.

9.8 A field trial was conducted at a contaminated site using the EnviroGard™ PCP in Soil test kit. Method 4010 was used to identify soil which had been contaminated with PCP from wood

treatment operations. A total of 33 samples were analyzed including 5 field duplicates. For the field duplicates, the reference method demonstrated an average coefficient of variation of 16%. For Method 4010 average coefficient of variation was 31%. Since Method 4010 is not quantitative, quantitative values were estimated. These data are shown in Table 9. At the 10 ppm cutoff, there were 0/33 (0%) false negatives and 0/33 (0%) false positives. At the 100 ppm cutoff, there was 1/33 (3%) false negatives and 1/33 (3%) false positives. These data are shown in Table 10.

10.0 REFERENCES

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TABLE 1A

Cross Reactivity for PCP PENTA RISc™ Test Kit

Compound[a]	Concentration (mg/Kg) in Soil to Cause a False Positive for PCP at 0.5 mg/Kg	Concentration (µg/L) in Water to Cause a False Positive for PCP at 5 µg/L
2,6-Dichlorophenol	700	600
2,3,4-Trichlorophenol	400	600
2,4,6-Trichlorophenol	16	100
2,4,5-Trichlorophenol	100	500
2,3,5,6-Tetrachlorophenol	1.2	7
Tetrachlorohydroquinone	500	>1500

[a] Compounds assayed at 3.75 µM (molar equivalent of PCP at 1000 µg/L), except where noted.

TABLE 1B

Cross Reactivity for PCP EnviroGard™ PCP in Soil Test Kit

Compound	Lower Limit of Detection (mg/kg)
Pentachlorophenol	10
2,5-Dichlorophenol	1000
2,6-Dichlorophenol	1000
2,3,4-Trichlorophenol	1000
2,3,5-Trichlorophenol	500
2,3,6-Trichlorophenol	500

TABLE 1B (cont.)

Compound	Lower Limit of Detection (mg/kg)
2,4,5-Trichlorophenol	500
2,4,6-Trichlorophenol	500
The following compounds were tested and found to yield negative results at 1,000 ppm:	
2,3,5,6-Tetrachloronitrobenzene 3,5-Dichlorophenol 2,4-Dichlorophenol 2,3-Dichlorophenol 4-Chlorophenol	PCB (Aroclor 1248) TNT DDT PAHs Chlordane

TABLE 2

Comparison of PENTA RISc™ Test Kit with GC/MS - Aqueous Matrix

Sample Type	Screening Results (ppm)							Concentration measured by GC/MS (ppm)	AGREEMENT[a] Y, FP, FN
	0.005	0.05	0.1	0.5	1	5	50		
groundwater					>	>	<	3.5	FP
			>	<				0.35	Y
	>	<						<0.1	Y
						>	<	8.2	Y
	>	>			>	<		2.8	Y
	>	>			>	<		2.9	Y
process water	>	>	<	<				0.21	FN
	>	>	<	<				0.17	Y
			>	<				0.12	Y
wastewater		>	>	<	<			0.6	FP
					>	<		1.4	Y
	>	>	<					<0.1	Y
			>	<				0.17	Y
run-off	>	>	<					<0.1	Y
	>	<						0.034	Y
		>			<			0.098	Y
		>			<			0.084	Y
		>			<			0.086	Y

TABLE 2 (cont.)

Sample Type	Screening Results (ppm)							Concentration measured by GC/MS (ppm)	AGREEMENT[a] Y, FP, FN
	0.005	0.05	0.1	0.5	1	5	50		
						>		2.1	FP
run-off (cont.)		>			<			0.073	Y
		>			<			0.026	FP
	>	<						0.006	Y
					>			0.169	FP
		>			<			0.239	Y
					>			0.190	FP
					>			0.114	FP
			>			<		0.346	Y
						>		1.1	Y
						>		19	Y
					>		<	4.3	Y

[a] Y = Yes, FN = False Negative, FP = False Positive

TABLE 3

Comparison of PENTA RISc™ Test Kit with GC/MS
Soil Matrix

Concentration measured by GC/MS (ppm)	Screening Results (ppm)			AGREEMENT[a] Y, FP, FN
	0.5	5	50	
1100	>	>	>	Y
88	>	>	<	FN
0.31	<	<	<	Y
0.72	<	<	<	FN
315	>	>	>	Y
1.5	>	<	<	Y
6.4	>	>	<	Y
9	>	>	<	Y
1.9	>	<	<	Y
46	>	>	>	FP
<1	>	<	<	Y
21	>	>	<	Y
3.3	>	<	<	Y
4	>	>	<	FP
11	>	>	<	Y
18	>	>	<	Y
33	>	>	<	Y
54	>	>	>	Y
65	>	>	>	Y
74	>	>	>	Y
83	>	>	>	Y
1.1	>	<	<	Y
14.3	>	>	<	Y
<1	<	<	<	Y
<1	<	<	<	Y

TABLE 3 (cont.)

Concentration measured by GC/MS (ppm)	Screening Results (ppm)			AGREEMENT[a] Y, FP, FN
	0.5	5	50	
<1	<	<	<	Y
3.9	>	<	<	Y
<1	<	<	<	Y
1.4	>	<	<	Y
48	>	>	>	FP
<1	<	<	<	Y
142	>	>	>	Y
108	>	>	<	FN
117	>	>	>	Y
56	>	>	>	Y
2.5	>	<	<	Y
3.5	>	>	<	FP
143	>	>	>	Y
nd	<	<	<	Y
0.02	<	<	<	Y
5	>	<	<	Y

Y = Yes, FN = False Negative, FP = False Positive.

TABLE 4

EnviroGard™ PCP in Soil Test Kit Sensitivity

Part 1 - Average Response with Negative Soils

Soil#	Soil Type	Average %Bo (n = 9)	Standard Deviation
S1	LOAM	97.6	3.0
S2	CLAY	100.1	1.4
S3	SAND	101.4	2.8
S4	LOAM	99.4	4.9
S5	SAND	100.2	3.1
S6	CLAY	97.4	2.7
S7	LOAM/SAND	102.6	0.3
S8	SAND/LOAM	97.5	3.6
AVERAGE		99.5	5.2

Part 2 - Average Response with Pentachlorophenol Calibrators

PCP Concentration (ppm)	Average Absorbance	Average %Bo
0	1.142	N/A
5	0.828	72.6
20	0.556	48.7
50	0.382	33.4
200	0.162	14.1

Part 3 - Method Sensitivity

Based on Part 1 and Part 2 Above:

Average %Bo - 2 SD = 89.2 which is equivalent to 1.6 ppm PCP

Average %Bo - 3 SD = 84.0 which is equivalent to 2.3 ppm PCP

(%Bo = [(ODsample/ODnegative control)x100])

TABLE 5

EFFECT OF WATER CONTENT IN SOIL SAMPLES[a]

Soil	% Water	Fortified?	Rep. 1	Rep. 2	Rep. 3	Mean	Std. Dev.	± 2 SD Range
S1	0	No	104.5*	106.5	99.7	103.6	3.5	96.6 - 111
S1	30	No	101.9	106.3	95.2	101.1	5.6	89.9 - 112
S1	0	Yes	38.9	47.2	40.2	42.1	4.4	33.3 - 50.9
S1	30	Yes	49.2	51.1	48.2	49.5	1.5	46.5 - 52.5
S2	0	No	97.8	105.7	96.7	100.1	4.9	90.3 - 110
S2	30	No	105.1	109.7	93.9	102.9	8.1	86.7 - 119
S2	0	Yes	40.2	47.5	42.7	43.5	3.7	36.1 - 50.9
S2	30	Yes	48.8	47.2	44.8	46.9	2.0	42.9 - 50.9
S3	0	No	98.3	107.1	99.7	101.7	4.7	92.3 - 111
S3	30	No	111.5	103.1	95.1	103.2	8.2	86.8 - 120
S3	0	Yes	43.3	47.2	43.2	44.6	2.3	40.0 - 49.2
S3	30	Yes	46.5	49.8	48.0	48.1	1.7	44.7 - 51.5

* All values shown are $\%Bo = [(OD_{sample}/OD_{negative\ control})x100]$

[a] EnviroGard™ PCP in Soil (Millipore, Inc.)

TABLE 6

EFFECT OF pH OF SOIL SAMPLES[a]

Soil	pH Adj.	Fortified?	Rep. 1*	Rep. 2	Rep. 3	Mean	Std. Dev.	± 2 SD Range
S1	None	No	103.1	98.6	98.6	100.1	2.6	94.9 - 105
S1	Acidic	No	88.7	96.9	100.2	95.3	5.9	83.5 - 107
S1	Basic	No	85.2	90.9	98.0	91.3	6.4	78.5 - 104
S1	None	Yes	52.7	44.8	45.8	47.8	4.3	39.2 - 56.4
S1	Acidic	Yes	57.1	44.6	45.2	48.9	7.0	34.9 - 62.9
S1	Basic	Yes	44.6	41.6	45.9	44.0	2.2	39.6 - 48.4
S2	None	No	105.6	93.9	102.5	100.7	6.1	88.5 - 113
S2	Acidic	No	104.4	91.3	105.8	100.5	8.0	84.5 - 117
S2	Basic	No	93.4	87.7	105.8	95.6	9.3	77.0 - 114
S2	None	Yes	47.8	45.1	44.3	45.7	1.8	42.1 - 49.3
S2	Acidic	Yes	51.4	44.4	54.1	50.0	5.0	40.0 - 60.0
S2	Basic	Yes	43.3	40.7	44.0	42.7	1.8	39.1 - 46.3
S3	None	No	92.3	101.8	100.4	98.2	5.2	87.8 - 109
S3	Acidic	No	96.6	91.9	98.5	95.7	3.4	88.9 - 103
S3	Basic	No	87.7	99.8	96.3	94.6	6.2	82.2 - 107
S3	None	Yes	55.2	49.5	55.9	53.6	3.5	46.6 - 60.6
S3	Acidic	Yes	55.3	48.3	42.0	48.5	6.7	35.1 - 61.9
S3	Basic	Yes	44.3	39.3	48.0	43.9	4.4	35.1 - 52.7

* All values shown are $\%Bo = [(OD_{sample}/OD_{negative\ control})x100]$

[a] EnviroGard™ PCP in Soil (Millipore, Inc.)

TABLE 7

TEST KIT[a] BIAS

Soil#	Fortification(ppm)	Extraction#	Recovered(ppm)*	% Recovery
S1	10	1	9	91
S1	10	2	9	86
S1	10	3	9	88
S1	100	1	84	84
S1	100	2	78	78
S1	100	3	76	76
Average >>				84
S2	10	1	10	100
S2	10	2	8	76
S2	10	3	8	76
S2	100	1	101	101
S2	100	2	98	98
S2	100	3	88	88
Average >>				90
S3	10	1	7	72
S3	10	2	8	76
S3	10	3	8	81
S3	100	1	95	95
S3	100	2	90	90
S3	100	3	87	87
Average >>				84

Overall Average %Recovery = 86

[a] EnviroGard™ PCP in Soil (Millipore, Inc.)

TABLE 8

EFFECT OF CO-CONTAMINATION WITH DIESEL OIL[a]

Soil#	Adulterated	Fortified	Rep.#1	Rep.#2	Rep.#3	Mean
S1	NO	NO	103.2*	92.5	99.8	98.5
S1	YES	NO	93.4	99.4	106.2	99.7
S1	NO	YES	52.7	44.8	45.8	47.8
S1	YES	YES	50.9	49.7	44.6	48.4
S2	NO	NO	103.1	98.3	102.3	101.2
S2	YES	NO	85.4	95.1	99.9	93.5
S2	NO	YES	47.8	45.1	44.3	45.7
S2	YES	YES	44.6	50.8	49.0	48.1
S3	NO	NO	98.9	95.4	108.1	100.8
S3	YES	NO	103.8	99.7	101.4	101.6
S3	NO	YES	55.2	49.5	55.9	53.6
S3	YES	YES	50.4	50.6	56.7	52.6

* Figures are %Bo = $[(OD_{sample}/OD_{negative\ control})*100]$

[a] EnviroGard™ PCP in Soil (Millipore, Inc.)

TABLE 9

FIELD DUPLICATES[a]

	Sample ID				
	059	073	074	086	087
Method 8270					
Determination #1	9600	74.8	836	6.59	34.0
Determination #2	10300	78.2	1520	6.88	51.8
Average	9950	76.5	1178	6.74	42.9
Standard Deviation	495	2.4	484	0.20	12.6
% Coefficient of Variation	5.0	3.1	41	3.0	29
Immunoassay*					
Determination #1	4480	79.5	604	2.4	36.0
Determination #2	3370	122	421	5.0	24.0
Average	3920	101	512	3.7	30.0
Standard Deviation	785	30.0	129	1.8	8.5
% Coefficient of Variation	20	30	25	50	28

* For the purpose of this comparison, quantitative values were calculated for the immunoassay.

[a] EnviroGard™ PCP in Soil (Millipore, Inc.)

TABLE 10

IMMUNOASSAY[a] COMPARED TO METHOD 8270
TEST INTERPRETATION AT 10 PPM PCP

Sample ID	Method 8270	Immunoassay	Concurrence?
059	9600	>10	YES
059D	10300	>10	YES
060	1010	>10	YES
061	2740	>10	YES
063	1610	>10	YES
064	1980	>10	YES
065	1580	>10	YES
066	57.8	>10	YES
067	110	>10	YES
068	47.7	>10	YES
069	798	>10	YES
070	2890	>10	YES
071	289	>10	YES
072	326	>10	YES
073	74.8	>10	YES
073D	78.2	>10	YES
074	836	>10	YES
074D	1520	>10	YES
075	3690	>10	YES
076	4590	>10	YES
077	2040	>10	YES
078	1720	>10	YES
079	792	>10	YES
080	2550	>10	YES
081	125	>10	YES
082	2400	>10	YES
083	270	>10	YES
084	1140	>10	YES
085	57.7	>10	YES
086	6.59	<10	YES
086D	6.88	<10	YES
087	34.0	>10	YES
087D	51.8	>10	YES

[a] EnviroGard™ PCP in Soil (Millipore, Inc.)

TABLE 10 (cont.)

Sample ID	Method 8270	Immunoassay	Concurrence?
059	9600	>100	YES
059D	10300	>100	YES
060	1010	>100	YES
061	2740	>100	YES
063	1610	>100	YES
064	1980	>100	YES
065	1580	>100	YES
066	57.8	<100	YES
067	110	>100	YES
068	47.7	<100	YES
069	798	>100	YES
070	2890	>100	YES
071	289	>100	YES
072	326	>100	YES
073	74.8	<100	YES
073D	78.2	>100	False Positive
074	836	>100	YES
074D	1520	>100	YES
075	3690	>100	YES
076	4590	>100	YES
077	2040	>100	YES
078	1720	>100	YES
079	792	>100	YES
080	2550	>100	YES
081	125	<100	False Negative
082	2400	>100	YES
083	270	>100	YES
084	1140	>100	YES
085	57.7	<100	YES
086	6.59	<100	YES
086D	6.88	<100	YES
087	34.0	<100	YES
087D	51.8	<100	YES

[a] EnviroGard™ PCP in Soil (millipore, Inc.).

METHOD 4015

SCREENING FOR 2,4-DICHLOROPHENOXYACETIC ACID BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4015 is a procedure for screening soils and aqueous matrices to determine whether 2,4-dichlorophenoxyacetic acid (2,4-D) (CAS Registry 94-75-7) is likely to be present at concentrations above 0.1, 0.5, 1.0 or 5.0 mg/kg in soil, and in aqueous matrices above 10 mg/L (the toxicity characteristic regulatory action level) and 10 µg/L (ground water monitoring). Method 4015 provides an estimate for the concentration of 2,4-D by comparison against standards.

1.2 Using the test kit from which this method was developed, ≥95% of aqueous samples confirmed to have concentrations of 2,4-D below detection limits will produce a negative result in the 10 ppm test configuration.

1.3 In cases where the exact concentration of 2,4-D is required, additional techniques (i.e., gas chromatography, Method 8151, or high performance liquid chromatography, Method 8321) should be used.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed.

2.2 In general, the method is performed using an extract of a soil sample, or directly on an aqueous sample. Filtered extracts may be stored cold, in the dark. An aliquot of the aqueous sample or extract and an enzyme-2,4-D conjugate reagent are added to immobilized 2,4-D antibody. The enzyme-2,4-D conjugate "competes" with 2,4-D present in the sample for binding to 2,4-D antibody. The enzyme-2,4-D conjugate bound to the 2,4-D antibody then catalyzes a colorless substrate to a colored product. The test is interpreted by comparing the color produced by a sample to the response produced by a reference reaction.

3.0 INTERFERENCES

3.1 Compounds that are chemically similar may cause a positive test (false positive) for 2,4-D. The data for the lower limit of detection of these compounds are provided in Tables 1A and 1C. Consult the information provided by the manufacturer of the kit used for additional information regarding cross reactivity with other compounds.

Solutions of Silvex alone, and Silvex/2,4-D mixtures, were prepared in TCLP buffer to demonstrate the potential effect of a structurally similar, environmentally significant cross-reactant on the immunoassay screening results. At one-half of the action level for 2,4-D (5ppm), 200 ppm of Silvex are required to be present to generate a false positive response. These results are summarized in Table 1B.

3.2 Storage and use temperatures may modify the method performance. Follow the manufacturer's directions for storage and use.

4.0 APPARATUS AND MATERIALS

Immunoassay test kit: 2,4-D RaPID$_{TM}$ Assay kit (Ohmicron), EnviroGard$_{TM}$ 2,4-D in Soil (Millipore, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Soil samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance specifications indicated in Tables 2-9.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Method 4000 and Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other test kits.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4015 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 Sensitivity of the EnviroGard™ 2,4-D in Soil Test Kit was determined by establishing the "noise" level expected from matrix effects encountered in negative soil samples and determining the corresponding 2,4-D concentration by comparison to the analyte-specific response curve. Eight different soils which did not contain 2,4-D were assayed. Each of these soils was extracted in triplicate and each extract was assayed in three different assays. The mean and the standard deviation of the resulting %Bo's (%Bo = [(OD_{sample}/$OD_{negative\ control}$)x100]) were calculated and the sensitivity was estimated at two standard deviations below the mean. The sensitivity for Method 4015 was determined to be 80% Bo at a 95% confidence interval. Based on the average assay response to 2,4-D, this corresponds to 0.16 ppm 2,4-D. These data are shown in Table 2.

9.2 The effect of water content of the soil samples was determined by assaying three different soil samples which had been dried and subsequently had water added to 30% (w/w). Aliquots of these samples were then fortified with 2,4-D. Each soil sample was assayed three times, with and without added water, and with and without 2,4-D fortification. It was determined that water in soil up to 30% had no detectable effect on the method. These data are shown in Table 3.

9.3 The effect of the pH of the soil extract was determined by adjusting the soil pH of three soil samples. Soil samples were adjusted to pH 2 - 4 using 6N HCl and pH 10 - 12 using 6N NaOH. Aliquots of the pH adjusted soil samples were fortified with 2,4-D. Each soil sample was assayed unadjusted and with pH adjusted to 2-4 and 10-12, both unfortified and fortified. It was determined that soil samples with pH ranging from 3 to 11 had no detectable effect on the performance of the method. These data are shown in Table 4.

9.4 The method bias was estimated by fortifying three different soil samples at two different concentrations (0.3 and 2 ppm 2,4-D). Each fortified sample was extracted three times and each extract was assayed three times. Recovery for individual determinations ranged from 27% to 151%. Average recovery for each individual extract ranged from 70% to 120%. Overall average recovery for all samples was 99.7%. These data are summarized in Table 5.

9.5 The probabilities of generating false negative and false positive results at a 10 ppm action level are shown in Table 6.

9.6 The results obtained from spiking 2,4-D into TCLP leachates and other aqueous samples are reported in Table 7. Each matrix was diluted 1:1000 and tested by immunoassay 5 times. The results are reported as positive (+) or negative (-). Municipal water results are based on a 52 ppb cutoff to determine positive from negative, and were diluted 1:7.

9.7 Comparison of the results from immunoassay and GC (Method 8151) testing of aqueous samples are presented in Table 8.

9.8 A field trial was undertaken to evaluate the ability of the EnviroGard™ 2,4-D in Soil Test Kit to identify 2,4-D contaminated soil at a remediation site. A total of 30 soil samples were evaluated by both the immunoassay and Method 8151. Interpretation of the results at 200 µg/kg resulted in 0/32 (0%) false negatives and 1/32 (3%) false positives. This corresponds to specificity 95% and sensitivity of 100%. These data are shown in Table 9.

10.0 REFERENCES

1. 2,4-D RaPID™ Assay kit Users Guide, Ohmicron.

2. EnviroGard™ 2,4-D in Soil Test Kit Guide, Millipore, Inc.

3. Lawruk, T.S., Hottenstein, C.S., Fleeker, J.R., Hall, J.C., Herzog, D.P., Rubio, F.M., "Quantitation of 2,4-D and Related Chlorophenoxy Herbicides by A Magnetic Particle-Based ELISA"' 1993, (manuscript submitted for publication).

4. Hayes, M.C., Jourdan, S.W., Lawruk, T.S., and Herzog, D.P., "Screening of TCLP Extracts of Soil and Wastewater for 2,4-D by Immunoassay", USEPA Ninth Annual Waste Testing and Quality Assurance Symposium, 1993.

TABLE 1A

CROSS-REACTIVITY[a] OF CHLOROPHENOXY COMPOUNDS AND STRUCTURALLY UNRELATED PESTICIDES

Compound	Concentration Giving a Positive Result (ppm TCLP Leachate)	Percent Cross-Reactivity
2,4-D	10	100
2,4-D propylene glycol ester	0.52	1900
2,4-D ethyl ester	0.54	1850
2,4-D isopropyl	0.96	1040
2,4-D methyl ester	1.09	917
2,4-D sec-butyl ester	1.40	714
2,4-D butyl ester	1.60	625
2,4-D butoxyethyl ester	2.00	500
2,4,5-T methyl ester	12.0	86
2,4-D iso-octyl ester	20.0	50
2,4-D butoxy-propylene ester	20.6	49
2,4-DB	95	11
MCPA	110	9
2,4,5-T	130	8
Silvex methyl ester	665	1.5
4-Chlorophenoxyacetic acid	815	1.2
MCPB	980	1.0
Silvex (2,4,5-TP)	1375	0.7
Dichlorophenol	2380	0.4
Dichloroprop	5000	0.2
Triclopyr	>10,000	<0.1
MCPP	>10,000	<0.1
Mecoprop	>10,000	<0.1
Pentachlorophenol	>10,000	<0.1
Picloram	>10,000	<0.1

TABLE 1A (cont.)

CROSS-REACTIVITY[a] OF CHLOROPHENOXY COMPOUNDS AND STRUCTURALLY UNRELATED PESTICIDES

Compound	Concentration Giving a Positive Result (ppm TCLP Leachate)	Percent Cross-Reactivity
Alachlor	>10,000	<0.1
Aldicarb	>10,000	<0.1
Aldicarb sulfate	>10,000	<0.1
Aldicarb sulfoxide	>10,000	<0.1
Atrazine	>10,000	<0.1
Benomyl	>10,000	<0.1
Butylate	>10,000	<0.1
Captan	>10,000	<0.1
Captofol	>10,000	<0.1
Carbaryl	>10,000	<0.1
Carbofuran	>10,000	<0.1
Dicamba	>10,000	<0.1
1,3-Dichloropropene	>10,000	<0.1
Dinoseb	>10,000	<0.1
Metolachlor	>10,000	<0.1
Metribuzin	>10,000	<0.1
Simazine	>10,000	<0.1
Terbufos	>10,000	<0.1
Thiabendazol	>10,000	<0.1

[a] 2,4-D RaPID™ Assay kit

TABLE 1B

CROSS-REACTIVITY[a] OF 2,4-D WITH SILVEX

Silvex Concentration (ppm)	2,4-D Concentration (ppm)	Screening Result
0	0	-
0.5	0	-
1.0	0	-
2.0	0	-
100	0	-
200	0	-
0	5.0	-
0.5	5.0	-
1.0	5.0	-
2.0	5.0	-
100	5.0	-
200	5.0	+

[a] 2,4-D RaPID™ Assay kit

TABLE 1C

CROSS REACTIVITY[a]

Compound	Concentration Required for Positive Interpretation (ppm)
2,4-D Acid	0.2
2,4-D butyl ester	0.025
2,4-D Dichlorophenol	1.5
2,4-D isobutyl ester	0.2
2,4-D isopropyl ester	0.2
2,4-D methyl ester	0.1
2,4-DB	0.2
2,4-DB butyl ester	0.9
Dichloroprop	6.0
Diclofop	42.5
MCPA	0.8
2,4,5-T acid	7.0

[a] EnviroGard™ 2,4-D in Soil Test Kit (Millipore Corporation)

TABLE 2

Sensitivity of the EnviroGard™ 2,4-D in Soil Test Kit

Part 1 - Average Response with Negative Soils			
Soil#	Soil Type	Average %Bo (n=9)	Standard Deviation
S1	LOAM	90.0	1.7
S2	LOAM	89.6	2.3
S3	SAND/LOAM	89.3	2.1
S4	CLAY	86.3	1.9
S5	CLAY	90.0	2.3
S6	LOAM/SAND	86.9	2.6
S7	SAND	88.8	2.8
	LOAM	86.9	2.9
Average		88.5	6.5
Part 2 - Average Response with 2,4-D Calibrators			
2,4-D Calibrator Concentration (ppm)		Average Absorbance	Average %Bo
0		1.442	N/A
0.1		1.186	82.2
0.5		0.776	53.8
1.0		0.600	41.7
5.0		0.301	20.9
Part 3 - Method Sensitivity			
Based on Part 1 and Part 2 Above:			
Average %Bo - 2 SD = 75.6 which is equivalent to 0.16 ppm 2,4-D			
Average %Bo - 3 SD = 69.1 which is equivalent to 0.23 ppm 2,4-D			

(%Bo = [(OD_{sample}/$OD_{negative\ control}$)x100])

TABLE 3

Effect of Water Content of Soil Samples on the EnviroGard™
2,4-D in Soil Test Kit

Soil	% Water	Fortified?	Rep. 1	Rep. 2	Rep. 3	Mean	Std. Dev.	± 2 SD Range
S1	0	No	98.7*	99.9	102.9	100.5	2.2	96.1 - 105
S1	30	No	96.0	95.4	93.7	95.0	1.2	92.6 - 97.4
S1	0	Yes	61.4	62.0	73.1	65.5	6.6	52.3 - 78.7
S1	30	Yes	63.1	59.9	69.4	64.1	4.8	54.5 - 73.7
S2	0	No	98.5	90.7	97.8	95.7	4.3	87.1 - 104
S2	30	No	96.0	95.4	96.8	96.1	0.7	94.7 - 97.5
S2	0	Yes	47.6	47.0	46.0	46.9	0.8	45.3 - 48.5
S2	30	Yes	37.6	37.7	40.0	38.4	1.3	35.8 - 41.0
S3	0	No	98.7	94.1	105.2	99.4	5.6	88.2 - 111
S3	30	No	97.3	97.2	95.9	96.8	0.8	95.2 - 98.4
S3	0	Yes	41.0	39.3	48.8	43.1	5.1	32.9 - 53.3
S3	30	Yes	43.1	40.4	47.4	43.6	3.5	36.6 - 50.6

* All values shown are $\%Bo = [(OD_{sample}/OD_{negative\ control})x100]$

TABLE 4

Effect of pH of Soil Samples on the EnviroGard™ 2,4-D in Soil Test Kit

Soil	pH Adj.	Fortified?	Rep. 1*	Rep. 2	Rep. 3	Mean	Std. Dev.	± 2 SD Range
S1	None	No	95.5	92.5	88.7	92.2	3.4	85.4 - 99.0
S1	Acidic	No	102	105	93.1	100	6.2	87.6 - 112
S1	Basic	No	96.8	98.3	79.4	91.5	10.5	70.5 - 113
S1	None	Yes	46.0	47.5	48.6	47.4	1.3	44.8 - 50.0
S1	Acidic	Yes	50	51.9	43.7	48.5	4.3	39.9 - 57.1
S1	Basic	Yes	43.0	52.4	39.1	44.8	6.8	31.2 - 58.4
S2	None	No	94.3	90.6	90.8	91.9	2.1	87.7 - 96.1
S2	Acidic	No	91.7	95.8	85.9	91.1	5.0	81.1 - 101
S2	Basic	No	89.7	94.2	81.0	88.3	6.7	74.9 - 102
S2	None	Yes	50.5	52.6	50.2	51.1	1.3	48.5 - 53.7
S2	Acidic	Yes	56.3	58.1	44.3	52.9	7.5	37.9 - 67.9
S2	Basic	Yes	46.9	54.2	46.4	49.1	4.4	40.3 - 57.9
S3	None	No	82.2	92.0	85.4	86.5	5.0	76.5 - 96.5
S3	Acidic	No	95.0	85.1	86.9	89.0	5.3	78.4 - 99.6
S3	Basic	No	86.1	84.4	103	91.2	10.4	70.4 - 112
S3	None	Yes	52.2	63.6	49.4	55.1	7.5	40.1 - 70.1
S3	Acidic	Yes	55.2	59.5	66.6	60.4	5.8	48.8 - 72.0
S3	Basic	Yes	59.4	54.3	54.9	56.2	2.8	50.6 - 61.8

* All values shown are $\%Bo = [OD_{sample}/OD_{negative\ control})x100]$

TABLE 5

Bias of the EnviroGard™ 2,4-D in Soil Test Kit

Soil#	Fortification (ppm)	Extraction#	Recovered (ppm)*	% Recovery
S1	0.3	1	0.21	70.0
S1	0.3	2	0.24	80.0
S1	0.3	3	0.23	76.6
S1	2	1	1.87	93.5
S1	2	2	2.12	106
S1	2	3	2.40	120
Average >>>				91.0
S2	0.3	1	0.29	96.7
S2	0.3	2	0.29	96.7
S2	0.3	3	0.30	100
S2	2	1	2.05	102
S2	2	2	1.89	94.5
S2	2	3	2.22	111
Average >>>				100
S3	0.3	1	0.31	103
S3	0.3	2	0.31	103
S3	0.3	3	0.31	103
S3	2	1	2.28	114
S3	2	2	2.30	115
S3	2	3	2.24	112
Average >>>				108

Overall Average %Recovery = 99.7

TABLE 6

Probability of False Negative and False Positive Results for 2,4-D RaPID™ Assay Kit at a 10 ppm Action Level in TCLP Extract from Organic Soil

Spike Concentration 2,4-D (ppm)	Probability of False Positive (%)	Probability of False Negative (%)
5	0	N/A
7.5	70	N/A
10	N/A	0
15	N/A	0

Results were based on ten replicate spiked samples. Cutoff levels were established using 30 replicates of each solution tested in 3 immunoassay batch runs.

N/A = No false positives possible above/below the action limit.

TABLE 7

2,4-D SPIKING RESULTS ON AQUEOUS ENVIRONMENTAL MATRICES[a]

ID #	Matrix+Spike	R1	R2	R3	R4	R5	%POS	%NEG
1	TCLP Buffer	-	-	-	-	-	-	-
2	TCLP Buffer + 15 ppm	+	+	+	+	+	+	+
3	TCLP Buffer + 10 ppm	+	+	+	+	+	+	+
4	TCLP Buffer + 5 ppm	-	-	-	-	-	-	-
5	Sandy Extract[b]	-	-	-	-	-	-	-
6	Sandy Extract + 15 ppm	+	+	+	+	+	+	+
7	Sandy Extract + 10 ppm	+	+	+	+	+	+	+
8	Sandy Extract + 5 ppm	-	-	-	-	-	-	-
9	Organic Extract[c]	-	-	-	-	-	-	-
10	Organic Extract + 15	+	+	+	+	+	+	+
11	Organic Extract + 10	+	+	+	+	+	+	+
12	Organic Extract + 5	-	-	-	-	-	-	-
13	Effluent #1	-	-	-	-	-	-	-
14	Effluent #1 + 15 ppm	+	+	+	+	+	+	+
15	Effluent #1 + 10 ppm	+	+	+	+	+	+	+
16	Effluent #1 + 5 ppm	-	-	-	-	-	-	-
17	Effluent #2	-	-	-	-	-	-	-
18	Effluent #2 + 15 ppm	+	+	+	+	+	+	+
19	Effluent #2 + 10 ppm	+	+	+	+	+	+	+
20	Effluent #2 + 5 ppm	-	-	-	-	-	-	-
21	Runoff	-	-	-	-	-	-	-
22	Runoff + 15 ppm	+	+	+	+	+	+	+
23	Runoff + 10 ppm	+	+	+	+	+	+	+
24	Runoff + 5 ppm	-	-	-	-	-	-	-
25	Municipal Water	-	-	-	-	-	-	-
26	Municipal Water + 140 ppb	+	+	+	-	-	-	-

TABLE 7 (cont.)

2,4-D SPIKING RESULTS ON AQUEOUS ENVIRONMENTAL MATRICES[a]

ID #	Matrix+Spike	R1	R2	R3	R4	R5	%POS	%NEG
27	Municipal Water + 70 ppb	+	+	+	-	-	-	-
28	Municipal Water + 35 ppb	-	-	-	-	-	-	-

[a] 2,4-D RaPID$_{TM}$ Assay kit

[b] Sandy Soil TCLP Extract

[c] Organic Soil TCLP Extract

TABLE 8

2,4-D Spiking Results
2,4-D RaPID™ Assay Kit vs. Method 8151

ID#	Matrix/Spike	Immunoassay Results	Method 8151 2,4-D (ppm)	Correlation IA vs. GC
1	TCLP Buffer	5/5 Negative	nd	Yes
2	TCLP Buffer + 15 ppm	5/5 Positive	13.0	Yes
3	TCLP Buffer + 10 ppm	5/5 Positive	11.0	Yes
4	TCLP Buffer + 5 ppm	5/5 Negative	5.6	Yes
5	Sandy Extract[a]	5/5 Negative	nd	Yes
6	Sandy Extract + 15 ppm	5/5 Positive	*	*
7	Sandy Extract + 10 ppm	5/5 Positive	5.9, 5.2	No
8	Sandy Extract + 5 ppm	5/5 Negative	*	*
9	Organic Extract[b]	5/5 Negative	nd	Yes
10	Organic Extract + 15 ppm	5/5 Positive	*	*
11	Organic Extract + 10 ppm	5/5 Positive	10.0, 9.5	Yes
12	Organic Extract + 5 ppm	5/5 Negative	*	*
13	Effluent #1	5/5 Negative	*	*
14	Effluent #1 + 15 ppm	5/5 Positive	*	*
15	Effluent #1 + 10 ppm	5/5 Positive	11.0, 7.8	Yes
16	Effluent #1 + 5 ppm	5/5 Negative	3.6	Yes
17	Effluent #2	5/5 Negative	*	*
18	Effluent #2 + 15 ppm	5/5 Positive	11.0	Yes
19	Effluent #2 + 10 ppm	5/5 Positive	8.8, 9.5	Yes
20	Effluent #2 + 5 ppm	5/5 Negative	*	*
21	Runoff	5/5 Negative	nd	Yes
22	Runoff + 15 ppm	5/5 Positive	*	*
23	Runoff + 10 ppm	5/5 Positive	9.7, 8.6	Yes
24	Runoff + 5 ppm	5/5 Negative	5.5	Yes
25	Municipal Water	5/5 Negative	nd	N/A

TABLE 8 (cont.)

ID#	Matrix/Spike	Immunoassay Results	Method 8151 2,4-D (ppm)	Correlation IA vs. GC
26	Municipal Water + 140 ppb	5/5 Positive	*	N/A
27	Municipal Water + 70 ppb	5/5 Positive	58.59 (ppb)	N/A
28	Municipal Water + 35	5/5 Negative	*	N/A

[a] Sandy Soil TCLP Extract

[b] Organic Soil TCLP Extract

nd non-detectable

N/A Not applicable to wastewater regulatory limit

* No analysis with Method 8150

TABLE 9

Comparison of the EnviroGard™ 2,4-D in Soil Test Kit to Method 8151
Interpretation of Results at 200 µg/kg

Sample #	Method 8151, µg/kg	Immunoassay Result	Agrees?
1	<200	NEGATIVE	YES
2	<200	NEGATIVE	YES
3	220	POSITIVE	YES
4	<200	NEGATIVE	YES
5	<200	NEGATIVE	YES
6	330	POSITIVE	YES
7	<200	POSITIVE	FALSE POSITIVE
8	<200	NEGATIVE	YES
9	830	POSITIVE	YES
10	<200	NEGATIVE	YES
11	310	POSITIVE	YES
12	350	POSITIVE	YES
13	<200	NEGATIVE	YES
14	<200	NEGATIVE	YES
15	200	POSITIVE	YES
16	<200	NEGATIVE	YES
17	<200	NEGATIVE	YES
18	440	POSITIVE	YES
19	560	POSITIVE	YES
20	380	POSITIVE	YES

TABLE 9 (cont.)

Sample #	Method 8151, µg/kg	Immunoassay Result	Agrees?
21	<200	NEGATIVE	YES
22	360	POSITIVE	YES
23	<200	NEGATIVE	YES
24	<200	NEGATIVE	YES
25	<200	NEGATIVE	YES
26	<200	NEGATIVE	YES
27	<200	NEGATIVE	YES
28	<200	NEGATIVE	YES
29	<200	NEGATIVE	YES
30	<200	NEGATIVE	YES

METHOD 4020

SCREENING FOR POLYCHLORINATED BIPHENYLS BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4020 is a procedure for screening soils and non-aqueous waste liquids to determine when total polychlorinated biphenyls (PCBs) are present at concentrations above 5, 10 or 50 mg/kg. Method 4020 provides an estimate for the concentration of PCBs by comparison with a standard.

1.2 Using the test kit from which this method was developed, 95% of soil samples containing 0.625 ppm or less of PCBs will produce a negative result in the 5 ppm test configuration. Using another commercially available test kit, 97% of soil samples containing 0.25 ppm or less of PCBs will produce a negative result in the assay and greater than 99% of the samples containing 1.0 ppm or more will produce a positive result. Tables 2-5, 7, 10, and 11 present false positive and false negative data generated from commercially available test kits. Using a test kit commercially available for screening non-aqueous waste liquids, >95% of samples containing 0.2-0.5 ppm or less of PCB will produce a negative result.

1.3 In cases where the exact concentrations of PCBs are required, quantitative techniques (i.e., Method 8082) should be used.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed.

2.2 In general, the method is performed using a sample extract. Sample and an enzyme conjugate reagent are added to immobilized antibody. The enzyme conjugate "competes" with PCB present in the sample for binding to immobilized anti-PCB antibody.

2.3 The test is interpreted by comparing the response produced by testing a sample to the response produced by testing standard(s) simultaneously.

3.0 INTERFERENCES

Chemically similar compounds and compounds which might be expected to be found in conjunction with PCB contamination were tested to determine the concentration required to produce a positive test result. These data are shown in Tables 1A, 1B, 1C, and 1D.

4.0 APPARATUS AND MATERIALS

4.1 Immunoassay test kit: PCB RISc™ (EnSys, Inc.), EnviroGard™ PCB in Soil (Millipore, Inc.), D TECH ™ PCB test (Strategic Diagnostics Inc.), PCB RISc™ Liquid Waste Test System (EnSys, Inc.), or equivalent.

4.2 Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Also refer to Reference 9 for the collection and handling of non-aqueous waste liquids.

6.2 Samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

7.1 Follow the manufacturer's instructions for the test kit being used.

7.2 Those test kits used must meet or exceed the performance specifications indicated in Tables 2-11.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Method 4000 and Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other test kits.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4020 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 A study was conducted with the PCB RISc™ test kit using fourteen standard soils and three soil samples whose PCB concentration had been established by Method 8082. Replicates were performed on seven of the standard soils and on one of the soil samples for a total of 25 separate analyses. Each of two different analysts ran the 25 analyses. Results indicated that "<" assignments are accurate with almost 99% certainty at the 50 ppm level while ">" assignments can be up to about 96% inaccurate as the sample concentration approaches that of the testing level. Corresponding certainties at the 5 ppm level are 92% and 82% respectively. Tables 2 and 3 summarize these results.

9.2 Table 4 presents method precision data generated using the PCB RISc™ test kit, comparing immunoassay test results with results obtained using Method 8082.

9.3 Method precision was determined with the EnviroGard PCB in Soil test kit by assaying 4 different soils (previously determined to contain 5.04, 9.78, 11.8, and 25.1 mg/kg by Method 8082), at three different sites, using three different lots of assay kits, three times a day for 9 days. A total of 81 analyses were performed for each soil. Error attributable to site, lot, date, and operator were determined. Separately, the relative reactivity of Aroclors 1242, 1248, 1254, and 1260 were determined. Based on Aroclor heterogeneity, and method imprecision, concentrations of Aroclor 1248 were selected that would result in greater than 99% confidence for negative interpretation. A study was conducted (Superfund SITE demonstration) on 114 field samples whose PCB concentration were also determined by Method 8082. 32 of the field samples were collected in duplicate (as coded field duplicates) and assayed by standard and immunoassay methods. The results for all 146 samples are summarized in Tables 5 and 6.

9.4 Grab samples were obtained from sites in Pennsylvania, Iowa and Illinois using a stainless steel trowel. Each sample was homogenized by placing approximately six cubic inches in a stainless steel bucket and mixing with the trowel for approximately two minutes. The soils was aliquotted into 2 six ounce glass bottles. The samples were tested on site using the D TECH PCB test kit, and sent to an analytical laboratory for analysis by Method 8082. These data are compared in Table 7.

9.5 Tables 8 and 9 present data on the inter- and intra-assay precision of the PCB RISc™ Liquid Waste Test System. The data were generated using 11 samples, each spiked at 0, 0.2 and 5 ppm, and assayed 4 times.

9.6 Tables 10 and 11 provide data from application of the PCB RISc™ Liquid Waste Test System to a series of liquid waste samples whose PCB concentration had been established by Method 8082.

10.0 REFERENCES

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2. PCB RISc™ Users Guide, Ensys Inc.

3. R.W. Counts, R.R. Smith, J.H. Stewart, and R.A. Jenkins, "Evaluation of PCB Rapid Immunoassay Screen Test System", Oak Ridge National Laboratory, Oak Ridge, TN 37831, April 1992, unpublished

4. EnviroGard PCB in Soil Package Insert, Millipore Corp. 2/93.

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6. D TECH™ PCB Users Guide , SDI/Em Sciences

7. Melby, J.M., B.S. Finlin, A.B. McQuillin, H.G. Rovira, J.W. Stave, "PCB Analysis by Enzyme Immunoassay", Strategic Diagnostics Incorporated, Newark, Delaware, 1993

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9. T.A. Bellar and J.J Lichtenberg. The Analysis of Polychloringated Biphenyls in Transformer Fluid and Waste Oils. U.S. EPA Research and Development, EPA/EMSL-ORD, Cincinnati, Ohio (June 24, 1980). Revised June 1981, EPA 600/4-81-045.

10. PCB RISc™ Liquid Waste Test System, User's Guide, EnSys Environmental Products, Inc.

TABLE 1A

CROSS REACTIVITY OF DIFFERENT COMPOUNDS[a]

Compound	Soil Equivalent Concentration (ppm) Required to Yield a Positive Result
1-Chloronaphthalene	10,000
1,2,4-Trichlorobenzene	10,000
2,4-Dichlorophenyl-benzenesulfonate	1,000
2,4-Dichloro-1-naphthol	>10,000
Bifenox	500
Diesel fuel	>10,000
Pentachlorobenzene	>10,000
2,5-Dichloroaniline	>10,000
Hexachlorobenzene	>10,000
Gasoline	>10,000
Dichlorofenthion	10,000
Tetradifon	125

(a) PCB RISc™ test kit, Ensys, Inc. publication

TABLE 1B

CROSS REACTIVITY OF DIFFERENT COMPOUNDS[a]

Compound	% Cross Reactivity
Aroclor 1248	100
Aroclor 1242	50
Aroclor 1254	90
Aroclor 1260	50
1,2-, 1,3-, & 1,4-Dichlorobenzene	<0.5
1,2,4-Trichlorobenzene	<0.5
biphenyl	<0.5
2,4-dichlorophenol	<0.5
2,5-dichlorophenol	<0.5
2,4,5-trichlorophenol	<0.5
2,4,6-trichlorophenol	<0.5
Pentachlorophenol	<0.5

[a] EnviroGard PCB Test Kits (Millipore Corporation)

TABLE 1C

CROSS REACTIVITY OF DIFFERENT COMPOUNDS[a]

Compound	MDL[b] (ppm)	IC 50[c] (ppm)	% Cross Reactivity[d]
Aroclor 1016	5.7	83	12
Aroclor 1221	25.5	300	3
Aroclor 1232	9.0	105	10
Aroclor 1242	1.5	31	32
Aroclor 1248	0.8	24	42
Aroclor 1254	0.5	10	100
Aroclor 1260	0.75	10	100
Aroclor 1262	0.5	10	100
Aroclor 1268	3.8	40	25

METHOD: The compounds listed were assayed at various concentrations and compared against an inhibition curve generated using Aroclor 1254. The concentration of the compound required to elicit a positive response at the MDL as well as the concentration required to yield 50% inhibition compared to the standard curve were determined.

[a] D TECH™ PCB test kit

[b] The Minimum Detection Limit (MDL) is defined as the lowest concentration of compound that yields a positive test result.

[C] The IC_{50} is defined as the concentration of compound required to produce a test response equivalent to 50% of the maximum response.

[d] % Cross reactivity is determined by dividing the equivalent Aroclor 1254 concentration by the actual compound concentration at IC_{50}

TABLE 1D

CROSS REACTIVITY OF DIFFERENT COMPOUNDS[a]

Compound	% Cross-Reactivity	Soil Equivalent Concentration (ppm) Required to Yield a Positive Result
1-Chloronaphthalene	0.05%	10,000
1,2,4-Trichlorobenzene	0.05%	10,000
2,4-Dichloro-1-naphthol	<0.20%	>10,000
Bifenox	<0.10%	500
Pentachlorobenzene	<0.05%	>10,000
2,5-Dichloroaniline	<0.05%	>10,000
Hexachlorobenzene	<0.05%	>10,000
Dichlorofenthion	0.05%	10,000
Tetradifon	<0.10%	125

(a) PCB RISc™ Liquid Waste Test System, Ensys, Inc.

TABLE 2

ESTIMATED ERROR RATES FOR 5 PPM DILUTION[a]

True Value (ppm)	0	1	2	3	4	5	6	7	8	9	10	20
Estimated Rate of False Positives (%)	1.3	13.2	39.2	65.2	82.3	.	.	.	.	.	.	.
Estimated Rate of False Negatives (%)	.	.	.	.	.	8.5	4.1	2.0	1.0	0.5	0.3	<0.1

TABLE 3

ESTIMATED ERROR RATES FOR 50 PPM DILUTION[a]

True Value (ppm)	0	5	10	15	20	30	40	50	60	70	80	100
Estimated Rate of False Positives (%)	1.0	7.9	24.5	46.0	65.0	87.3	95.6	.	.	.	.	.
Estimated Rate of False Negatives (%)	.	.	.	.	.	.	.	1.7	0.7	0.3	0.2	<0.1

(a) PCB RISc™ test kit

TABLE 4

Comparison of PCB RISc™ Test Kit with GC

Sample ID	Screening Test Results	GC Results (Method 8082)	Agreement[a] Y, FP, FN
101	<5 ppm	<0.5 ppm	Y
284	<5 ppm	<0.5 ppm	Y
292	<5 ppm	<0.5 ppm	Y
199	<5 ppm	0.5 ppm	Y
264	<5 ppm	1 ppm	Y
257	<5 ppm	1.8 ppm	Y
259	<5 ppm	4 ppm	Y
265	<5 ppm	4.5 ppm	Y
200	<5 ppm	5 ppm	Y
170	5-50	5.8 ppm	Y
198	<5 ppm	2.2-5.8 ppm	Y
172	5-50	6.2 ppm	Y
169	5-50	7.2 ppm	Y
171	5-50	7.2 ppm	Y
202	<5 ppm, 5-50	1.3-7.2 ppm	Y
163	5-50	8.7 ppm	Y
165	5-50	9 ppm	Y
168	5-50	9 ppm	Y
166	5-50	9.3 ppm	Y
164	5-50	11.9 ppm	Y
204	5-50	12.8 ppm	Y
253	5-50	13 ppm	Y
203	5-50	13.5 ppm	Y
258	5-50	15 ppm	Y
106	5-50	15-19 ppm	Y
161	5-50	15.3 ppm	Y
167	5-50	16.2 ppm	Y

TABLE 4 (cont.)

Sample ID	Screening Test Results	GC Results (Method 8082)	Agreement[a] Y, FP, FN
247	5-50	18 ppm	Y
148	>50	18-34 ppm	FP
205	5-50	20 ppm	Y
162	5-50	20.4 ppm	Y
175	5-50	21.2 ppm	Y
176	5-50	21.6 ppm	Y
197	5-50	32 ppm	Y
243	5-50	32 ppm	Y
252	5-50	32 ppm	Y
178	5-50	43.7 ppm	Y
201	5-50	43 ppm	Y
254	5-50, >50	56 ppm	Y
238	>50	46-60 ppm	Y
248	5-50	44-60 ppm	Y
250	>50	68 ppm	Y
242	5-50	30-69 ppm	Y
256	>50	73 ppm	Y
249	>50	96 ppm	Y
245	>50	102 ppm	Y
241	5-50	154 ppm	FN
246	>50	154 ppm	Y
261	>50	204 ppm	Y
240	>50	251 ppm	Y
267	>50	339 ppm	Y
239	>50	460 ppm	Y
104	>50	200-3772 ppm	Y
108	>50	531-1450 ppm	Y

[a] Y=Yes, FN=False Negative, FP=False Positive

TABLE 5

Comparison of EnviroGard™ PCB Kit with GC

Sample Number	Screening Result[c,d]	GC Result[c] [8082]	Agreement[e] Y, FN, FP
001	>10	5.98	FP[g]
002	>10	1.27	FP
003	<10	0.11	Y
004	>10	6.71	FP[g]
005	>10	1.37	FP
006	>10	0.68	FP
007	>10	0.55	FP
008	>10	2.00	FP
009	>10	1.30	FP
010	>10	0.17	FP
011	>10	1.15	FP
012	<10	ND[f]	Y
013	<10	1.13	Y
014	<10	0.18	Y
015	>10	9.13	FP[g]
015	>10	9.84	FP[g]
016	>10	2110	Y
017	>10	2.55	FP
018	>10	45.4	Y
019	>10	6.70	FP[g]
020	<10	0.07	Y
021	<10	0.06	Y
022	<10	0.54	Y
022	<10	0.72	Y
023	>10	20.8	Y
024	<10	0.06	Y

TABLE 5 (cont.)

Sample Number	Screening Result[c,d]	GC Result[c] [8082]	Agreement[e] Y, FN, FP
024D	<10	0.05	Y
025	>10	11.7	Y
026	<10	1.96	Y
027	<10	0.06	Y
028	<10	0.22	Y
028D	<10	0.22	Y
029	<10	0.23	Y
030	<10	1.15	Y
031	<10	0.26	Y
032	>10	47.6	Y
033	>10	6.00	FP[g]
034	>10	34.0	Y
035	<10	ND[f]	Y
035D	<10	ND[f]	Y
036	>10	816	Y
037	<10	0.06	Y
037D	<10	0.04	Y
038	>10	1030	Y
039	<10	0.68	Y
040	>10	4.25	FP
041	<10	ND[f]	Y
042	>10	0.52	FP
042D	>10	0.47	FP
043	>10	1.69	FP
043D	>10	1.74	FP

TABLE 5 (cont.)

Sample Number	Screening Result[c,d]	GC Result[c] [8082]	Agreement[e] Y, FN, FP
044	<10	0.59	Y
045	<10	ND[f]	Y
046	<10	ND[f]	Y
046D	<10	ND[f]	Y
047	<10	0.09	Y
047D	<10	0.10	Y
048	<10	ND[d]	Y
049	<10	ND[d]	Y
050	>10	3.60	FP
050D	>10	4.41	FP
051	<10	ND[f]	Y
052	>10	4.21	FP
053	<10	0.96	Y
054	<10	0.52	Y
055	<10	2.40	Y
056	<10	0.51	Y
057	<10	ND[f]	Y
058	<10	0.69	Y
059	>10	7.86	FP[g]
060	>10	0.62	FP
060D	<10	0.58	Y
061	>10	580	Y
062	>10	2.35	FP
063	<10	0.09	Y
063D	<10	0.15	Y

TABLE 5 (cont.)

Sample Number	Screening Result[c,d]	GC Result[c] [8082]	Agreement[e] Y, FN, FP
064	>10	19.0	Y
065	>10	3.08	FP
066	<10	1.98	Y
067	<10	0.08	Y
068	<10	0.50	Y
069	<10	ND[f]	Y
069D	<10	ND[f]	Y
070	<10	ND[f]	Y
071	<10	0.05	Y
071D	<10	ND[f]	Y
072	<10	0.04	Y
073	>10	15.8	Y
074	>10	13.3	Y
075	>10	23.0	Y
076	>10	46.7	Y
077	<10	ND[f]	Y
078	>10	2.27	FP
079	>10	42.8	Y
080	<10	3.77	Y
081	<10	0.69	Y
081D	<10	0.45	Y
082	<10	ND[f]	Y
082D	<10	0.24	Y
083	<10	0.48	Y
083D	<10	0.41	Y
084	>10	1.16	FP

TABLE 5 (cont.)

Sample Number	Screening Result[c,d]	GC Result[c] [8082]	Agreement[e] Y, FN, FP
084D	>10	1.08	FP
085	>10	428	Y
085D	>10	465	Y
086	<10	1.42	Y
086D	<10	1.25	Y
087	<10	0.08	Y
087D	<10	ND[f]	Y
088	>10	2.70	FP
088D	>10	1.77	FP
089	>10	45.0	Y
090	<10	1.01	Y
090D	<10	1.40	Y
091	>10	1630	Y
091D	>10	1704	Y
092	<10	1.21	Y
092D	<10	ND[f]	Y
093	<10	0.30	Y
094	<10	0.36	Y
095	>10	17.5	Y
095D	>10	31.2	Y
096	<10	0.06	Y
097	<10	1.23	Y
097D	<10	0.29	Y
098	>10	1.17	FP
098D	>10	0.83	FP
099	<10	ND[f]	Y

TABLE 5 (cont.)

Sample Number	Screening Result[c,d]	GC Result[c] [8082]	Agreement[e] Y, FN, FP
100	>10	177	Y
100D	>10	167	Y
101	>10	1.21	FP
102	>10	293	Y
102D	>10	177	Y
103	>10	40.3	Y
104	>10	7.66	FP[g]
105	<10	0.21	Y
106	<10	2.50	Y
107	>10	14.1	Y
108	>10	3.84	FP
109	<10	ND[f]	Y
109D	<10	ND[f]	Y
110	<10	ND[f]	Y
111	<10	ND[f]	Y
112	>10	315	Y
113	>10	14.9	Y
114	>10	66.3	Y

[c] mg/kg (ppm)

[d] Screening Calibrator is 5 mg/kg Aroclor 1248

[e] Y=Yes, FN=False Negative, FP=False Positive

[f] ND = Not Detectable

[g] Expected Result Based on Calibrator Concentration

TABLE 6

EnviroGard™ PCB Kit Field Performance Summary

Specificity:	[1-(Reported Positives/True Negatives)] = [1-(37/109)] = 66%
Note 1:	8 of the 37 reported positive samples had PCB contamination levels between 5 and 10 mg/kg. Soils in this range should test "positive" because the assay calibrator is 5 mg/kg Aroclor 1248. A positive assay bias is necessary to prevent false negative results. Eliminating these samples from the calculations produces a Specificity of: [1-(Reported Positives/True Negatives)] = [1-(29/101)] = 71%
Note 2:	The distribution of false positives is not random ($p < 0.05$), with a clustering at the beginning of the sample set. This observation was included in *Developers Comments* which were added to the final draft of the Technical Evaluation Report. One explanation for the higher frequency of false positive results at the beginning is inexperience of the operator with the method. If the first 20 samples are eliminated from the Specificity analysis, the following result is obtained: [1-(Reported Positives/True Negatives)] = [1-(20/86)] = 77% In the SITE demonstration, the PCB Immunoassay had a 77% positive predictive value.
Sensitivity:	[1-(Reported Negatives/True Positives)] = [1-(0/31)] = 100% In the SITE demonstration, the PCB Immunoassay had a 100% negative predictive value.

TABLE 7

Comparison of D TECH™ PCB Test Kit with GC

Sample	D TECH™ (ppm)	GC (8082) (ppm)	Agreement[a] Y, FN, FP
J1	4.0-15	5.0	Y
J2	>50	147	Y
J3	15-50	54	Y
J5	15-50	160	FN
J6	>50	1200	Y
J7	4.0-15	12	Y
J8	4.0-15	28	FN
J9	>50	463	Y
J10	>50	1760	Y
J11	>50	28	FP
J12	15-50	17	Y
J13	>50	1300	Y
J14	>50	186	Y
J15	15-50	31	Y
J16	15-50	36	Y
J17	>50	31	FP
J18	>50	130	Y
J19	>50	1310	Y
J20	>50	2620	Y
J21	>50	111000	Y
J22	1.0-4.0	0.01	FP
J23	1.0-4.0	0.60	Y
J24	<0.5	0.10	Y

[a] Y=Yes, FN=False Negative, FP=False Positive

TABLE 7 (cont.)

Sample	D TECH™ (ppm)	GC (8082) (ppm)	Agreement[a] Y, FN, FP
J25	0.5-1.0	0.12	FP
J26	<0.5	0.01	Y
J27	1.0-4.0	1.8	Y
J28	<0.5	0.18	Y
J29	0.5-1.0	0.54	Y
J30	>50	21	FP
J31	4.0-15	13	Y
J32	0.5-1.0	0.72	Y
J33	0.5-1.0	0.32	Y
J34	1.0-4.0	0.36	FP
J35	1.0-4.0	0.26	FP
J36	>50	70	Y
J37	<0.5	0.12	Y
J38	0.5-1.0	0.81	Y
J39	0.5-1.0	0.33	Y
J40	<0.5	0.19	Y
J41	<0.5	0.01	Y
J42	1.0-4.0	0.43	FP
J43	1.0-4.0	0.31	FP
J44	15-50	503.4	FN
J45	15-50	5.6	FP
J46	<0.5	0.02	Y
J47	<0.5	0.22	Y

[a] Y=Yes, FN=False Negative, FP=False Positive

TABLE 7(cont.)

Sample	D TECH™ (ppm)	GC (8082) (ppm)	Agreement[a] Y, FN, FP
G1	15-50	18	Y
G2	4.0-15	11	Y
G3	1.0-4.0	3.4	Y
G4	15-50	6.5	FP
G5	<0.5	0.01	Y
G6	1.0-4.0	1.4	Y
G7	1.0-4.0	0.30	FP
G8	15-50	7.5	FP
G9	4.0-15	33	FN
G10	15-50	8	FP
G11	4.0-15	11	Y
G12	4.0-15	24	FN
G13	4.0-15	4.3	Y
G14	0.5-1.0	1.3	Y
G15	<0.5	0.01	Y
G16	1.0-4.0	3.2	Y
G17	4.0-15	18	Y
G18	4.0-15	4.6	Y
G19	1.0-4.0	2.3	Y
G20	>50	37	FP

[a] Y=Yes, FN=False Negative, FP=False Positive

TABLE 7(cont.)

Sample	D TECH™ (ppm)	GC (8082) (ppm)	Agreement[a] Y, FN, FP
W1A	4.0-15	9.1	Y
W2A	4.0-15	11	Y
W3A	1.0-4.0	2.8	Y
W4A	4.0-15	13	Y
W5A	>50	29	FP
W6A	>50	1200	Y
W7A	>50	57	Y
W8A	4.0-15	18	Y
W9A	1.0-4.0	1.3	Y
W10A	0.5-1.0	0.44	Y
W11A	15-50	120	FN
W12A	15-50	48	Y
W13A	15-50	19	Y
W14A	4.0-15	2.7	Y
W15A	1.0-4.0	1.3	Y
W16A	1.0-4.0	0.3	FP
W17A	4.0-15	1.4	FP
W18A	1.0-4.0	2.2	Y
W19A	4.0-15	8.2	Y
W20A	>50	9.3	FP
W21A	>50	110	Y
W22A	1.0-4.0	0.6	Y
W23A	>50	46	Y

[a] Y=Yes, FN=False Negative, FP=False Positive

TABLE 8

Intraassay Precision of the PCB RISc™ Liquid Waste Test System

PCB 1248 Spike Concentration (ppm)	Signal %RSD (OD_{450nm}) N=44 (11 data sets)	Statistical Percentage of False Results Compared to Standards
0	6.4%	<0.02%
0.2	5.9%	4.1%
5	7.9%	1.4%

TABLE 9

Interassay Precision of the PCB RISc™ Liquid Waste Test System

PCB 1248 Spike Concentration (ppm)	Signal %RSD (OD_{450nm}) N=44 (11 data sets)
0	6.4%
0.2	8.3%
5	8.5%

TABLE 10

Comparison of PCB RISc™ Liquid Waste Test with Method 8082

Sample ID	Sample Matrix	GC Results		IA Results	
		Aroclor	Conc. ppm	Test Results	Corr. with GC Results
302	Condensate	ND[b]	ND	<5	yes
303	Condensate	ND	ND	<5	yes
304	Condensate	1242	25	≥5	yes
306	Condensate	1242	5	≥5	yes
307	Condensate	1242	<10	<5	yes
308	Condensate	1242	58	≥5	yes
310	Condensate	1254	25	≥5	yes
311	Condensate	1242	200	≥5	yes
331	Transformer Oil	1260	183	≥5	yes
380	Transformer Oil	PCB[c]	20	≥5	yes
381	Transformer Oil	PCB	38	≥5	yes
382	Transformer Oil	PCB	163	≥5	yes
383	Transformer Oil	PCB	176	≥5	yes
384	Transformer Oil	PCB	336	≥5	yes
385	Transformer Oil	PCB	6400	≥5	yes
387	Coolant	PCB	10	≥5	yes
388	2,4-D Rinse Water	1254	<10	<5	yes
389	Waste Solvent	1242	29	≥5	yes
390	Herbicide	ND	<2	<5	yes
391	Paint/Solvent	1254	9	≥5	yes
394	Waste Solvent	1242/1260	11/17	≥5	yes
395	Waste Solvent	1242/1260	2/2	<5	yes
396	Waste Oil	1260	323	≥5	yes
398	Chlor. Solvent	ND	<5	<5	yes
399	Paint	ND	<50	<5	yes
400	Pump Oil	ND	<50	<5	yes
401	Waste Solvent	ND	<35	<5	yes
402	Herbicide	ND	<50	<5	yes
403	Paint/Solvent	ND	<5	<5	yes
404	Printing Solvent	ND	<5	<5	yes
405	Waste Solvent	ND	<50	<5	yes

TABLE 10 (cont.)

Sample ID	Sample Matrix	GC Results		IA Results	
		Aroclor	Conc. ppm	Test Results	Corr. with GC Results
407	Waste Oil	ND	ND	≥5	FP[d]
408	Waste Oil	ND	ND	<5	yes
409	Waste Oil	ND	ND	<5	yes
410	Waste Oil	ND	ND	<5	yes
411	Waste Oil	ND	ND	<5	yes
412	Waste Oil	ND	ND	<5	yes
413	Waste Oil	ND	ND	<5	yes
414	Waste Oil	ND	ND	<5	yes
415	Waste Oil	ND	ND	<5	yes
416	Waste Oil	PCB	50	>5	yes
417	Waste Oil	ND	ND	<5	yes
418	Waste Oil	ND	ND	<5	yes
419	Waste Oil	ND	ND	<5	yes
420	Waste Oil	ND	ND	<5	yes
421	Waste Oil	ND	ND	<5	yes
422	Waste Oil	ND	ND	<5	yes
423	Waste Oil	ND	ND	<5	yes
424	Waste Oil	ND	ND	<5	yes
425	Waste Oil	ND	ND	<5	yes
Number of False Positive Results				1/32	
Rate				3.1%	
Number of False Negative Results				0/18	
Rate				0.0%	

[a] Trial 1 data

[b] ND = Not Detectable

[c] PCB = Aroclor was not determined

[d] FP = False positive

TABLE 11

Correlation of PCB RISc™ Liquid Waste Test and Method 8082 Results
Using Spiked and Unspiked Liquid Waste Field Samples

ID	Matrix	GC Results Unspiked ppm	Immunoassay Result		Interp.
			Unspiked ppm	Spiked (5 ppm 1248)	
001	Aromatic solvent	<5	<5	≥5	
002	Aviation gas	<5	<5	≥5	
003	Chiller oil	<5	<5	≥5	
004	Compressor oil	<5	<5	≥5	
005	Coolant + water	<5	<5	≥5	
006	Coolant oil	NR[b]	NR	≥5	
007	Coolant oil	NR	<5	≥5	
008	Cutting oil	<5	<5	≥5	
009	Cutting oil	<5	<5	≥5	
010	Degreaser still bottom	<5	<5	≥5	
011	Dope oil	<5	<5	≥5	
012	Draw Lube oil	<5	<5	≥5	
013	Fleet crankcase oil	<5	<5	≥5	
014	Floor sealer	<5	<5	≥5	
015	Fuel oil	<5	<5	≥5	
016	Hi-BTU oil	<5	<5	≥5	
017	Honing oil	<5	<5	≥5	
018	Hydraulic oil	<5	<5	≥5	
019	Hydraulic oil	<5	<5	≥5	
020	Hydraulic oil	<5	<5	≥5	
021	Machine oil	NR	<5	NR	
022	Mineral oil	<5	<5	≥5	
023	Mineral spirits	<5	<5	≥5	
024	Mineral spirits + ink	<5	≥5	≥5	FP
025	Mixed flammables	<5	<5	≥5	
026	Mixed solvents	<5	<5	≥5	
027	Naphtha	<5	<5	≥5	
028	Oil	<5	<5	≥5	
029	Oil	<5	<5	≥5	
030	Oil	<5	<5	≥5	
031	Oil	<5	<5	≥5	

TABLE 11 (cont.)

ID	Matrix	GC Results Unspiked ppm	Immunoassay Result		Interp.
			Unspiked ppm	Spiked (5 ppm 1248)	
032	Oil	<5	<5	≥5	
033	Oil	<5	<5	≥5	
034	Oil + 1,1,1-trichloroethane	<5	<5	≥5	
035	Oil sludge	<5	≥5	≥5	FP
036	Oil + freon	<5	<5	≥5	
037	Oil + mineral spirits	<5	<5	≥5	
038	Oil + scum solution	<5	<5	≥5	
039	Oily water	<5	<5	≥5	
040	Paint thinner	<5	<5	≥5	
041	Paint thinner	<5	<5	≥5	
042	Paint thinner	<5	<5	≥5	
043	Paint waste	<5	<5	≥5	
044	Paint waste + thinner	<5	<5	≥5	
045	Perce + oil	<5	<5	≥5	
046	Petroleum distillates	<5	≥5	≥5	FP
047	Petroleum naphtha	<5	<5	≥5	
048	Pumping oil	<5	<5	≥5	
049	RAC-1 SKOS	<5	<5	≥5	
050	Sk oil	NR	<5	≥5	
051	Sk oil	<5	<5	≥5	
052	Smog Hog	<5	<5	≥5	
053	Toluene + hexane	<5	<5	≥5	
054	Toluene + stain	<5	<5	≥5	
055	1,1,1-Trichloroethane	<5	≥5	≥5	FP
056	1,1,1-Trichloroethane	<5	<5	≥5	
057	1,1,1-Trichloroethane	<5	<5	≥5	
058	1,1,1-Trichloroethane	<5	<5	≥5	
059	1,1,1-TCE + methanol	<5	<5	≥5	
060	Trichloroethylene	<5	<5	≥5	
061	Trichloroethylene	<5	<5	≥5	
062	Trichloroethylene	<5	<5	≥5	
063	Turpentine	<5	<5	≥5	

TABLE 11 (cont.)

ID	Matrix	GC Results Unspiked ppm	Immunoassay Result		Interp.
			Unspiked ppm	Spiked (5 ppm 1248)	
064	Used n-butylacetate	<5	<5	≥5	
065	Used oil + freon	<5	<5	≥5	
066	Used oil + freon	<5	<5	≥5	
067	Used oils	<5	<5	≥5	
068	Used petroleum	<5	<5	≥5	
069	Used petroleum	<5	<5	≥5	
070	Used synthetic oil	<5	<5	≥5	
071	Varnish + stain	<5	<5	≥5	
072	Varsol	<5	<5	≥5	
073	Waste coolant + oil	<5	<5	≥5	
074	Waste ink + solvent	<5	<5	≥5	
075	Waste naphtha	<5	<5	≥5	
076	Waste oil	<5	<5	≥5	
077	Waste oil	<5	<5	≥5	
078	Waste oil	<5	<5	≥5	
079	Waste oil	<5	<5	≥5	
080	Waste oil	<5	<5	≥5	
081	Waste oil	<5	<5	≥5	
082	Waste oil	<5	<5	≥5	
083	Waste oil	<5	<5	≥5	
084	Waste oil	<5	<5	≥5	
085	Waste oil + kerosene	<5	<5	≥5	
086	Waste oil + gas	<5	<5	≥5	
087	Waste paint	<5	<5	≥5	
088	Waste paint	<5	<5	≥5	
089	Waste paint	<5	<5	≥5	
090	Waste paint	<5	<5	≥5	
091	Waste paint	<5	<5	≥5	
092	Waste paint	<5	<5	≥5	FP
093	Waste SC-49 solvent	<5	<5	≥5	
094	Waste solvent	<5	<5	≥5	
095	Waste stoddard	<5	<5	≥5	
096	Waste toner	<5	<5	≥5	

TABLE 11 (cont.)

ID	Matrix	GC Results Unspiked ppm	Immunoassay Result		Interp.
			Unspiked ppm	Spiked (5 ppm 1248)	
097	Waste tramp oil	<5	<5	≥5	
098	Waste transmission fluid	<5	<5	≥5	
099	Xylene	<5	≥5	≥5	FP
100	Not Recorded	<5	<5	NR	
No. of False Positive Results		6/99			
Rate		6.1%			
No. of False Negative Results				0/98	
Rate				0.0%	

[a] Trial 2 data

[b] NR = not run

METHOD 4030

SOIL SCREENING FOR PETROLEUM HYDROCARBONS BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4030 is a procedure for screening soils to determine whether total petroleum hydrocarbons (TPH) are likely to be present. Depending on the testing product selected, samples may be used to locate samples with low (<40-100 ppm), medium, and high (>1000 ppm) concentrations of contaminates, or to determine if TPH is present at concentrations above 5, 25, 100, or 500 mg/kg. Method 4030 provides an estimate for the concentration of TPH by comparison against standards, and can be used to produce multiple results within an hour of sampling.

1.2 Using the test kit from which this method was developed, 95 % of samples containing 25 ppm or less of TPH will produce a negative result in the 100 ppm test configuration.

1.3 The sensitivity of any immunoassay test depends on the binding of the target analyte to the antibodies used in the kit. The testing product used to develop this method is most sensitive to the small aromatic compounds (e.g., ethylbenzene, xylenes, and naphthalene) found in fuels. Refer to the package insert of the testing product selected for specific information about sensitivity.

1.4 The sensitivity of the test is influenced by the nature of the hydrocarbon contamination and any degradation processes operating at a site. Although the action level of the test may vary from site to site, the test should produce internally consistent results at a particular site.

1.5 In cases where a more exact measurement of TPH concentration is required, additional techniques (i.e., gas chromatography Method 8015 or infra-red spectroscopy Method 8440) should be used.

1.6 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed.

2.2 In general, the method is performed using an extract of a soil sample. Filtered extracts may be stored cold, in the dark. An aliquot of the extract and an enzyme-TPH conjugate reagent are added to immobilized TPH antibody. The enzyme-TPH conjugate "competes" with hydrocarbons present in the sample for binding to immobilized anti-TPH antibody. The test is interpreted by comparing the response produced by a sample to the response produced by a reference reaction.

3.0 INTERFERENCES

3.1 Compounds that are chemically similar to petroleum hydrocarbons may cause a positive test (false positive) for TPH. The data for the lower limit of detection of these compounds are provided in Tables 1A and 1B. Consult the information provided by the manufacturer of the kit used for additional information regarding cross reactivity with other compounds.

3.2 Storage and use temperatures may modify the method performance. Follow the manufacturer's directions for storage and use.

3.3 Appropriate standards must be used (i.e., diesel standards for diesel analysis, JP-4 for analysis of JP-4, etc.), or excessive false negative or false positive rates may result.

4.0 APPARATUS AND MATERIALS

Immunoassay test kit: PETRO RISc Soil Test (EnSys, Inc.), EnviroGard™ Petroleum Fuels in Soil, (Millipore, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Soil samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

7.1 Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance specifications indicated in Tables 2-12.

7.2 Appropriate standards must be used to prevent excessive rates of false negative or false positive results.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Method 4000 and Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other test kits.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4030 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 A single laboratory study was conducted with the PETRO RISc Soil Test, EnSys, Inc., using five contaminated soil samples. The samples were contaminated with oxygenated gasoline, oxygenated gasoline 24 hours after contamination, low aromatic diesel (purchased in California), normal diesel (purchased in Northern Virginia), and JP-4 jet fuel. Five replicate determinations were made using the kits, and the data compared with values obtained using GC/FID (Method 8015) and IR (Method 8440). Several different analysts ran the immunoassay analyses. Samples two- to five-fold below the action level generally gave readings less than the action level. Samples two fold above the action level gave readings greater than the action level. Samples at or near the action level give mixed results (e.g., both less than and greater than the action level). Tables 2 - 6 summarize these results.

9.2 Sensitivity of the EnviroGard Petroleum Fuels in Soil Test Kit was determined by establishing the "noise" level expected from matrix effects encountered in negative soil samples and determining the corresponding TPH concentration by comparison to the analyte-specific response curve. 8 different soils which did not contain TPH were assayed. Each of these soils was extracted in triplicate and each extract was assayed in three different assays. The mean and the standard deviation of the resulting %Bo's (%Bo = $[(OD_{sample}/OD_{negative\ control})x100]$) were calculated and the sensitivity was estimated at two standard deviations below the mean. The sensitivity for Method 4030 was determined to be 80% Bo at a 95% confidence interval. Based on the average assay response to home heating oil (HHO), this corresponds to 5.8 ppm. These data are shown in Table 7.

9.3 The effect of water content of the soil samples was determined by assaying three different soil samples which had been dried and subsequently had water added to 30% (w/w). Aliquots of these samples were then fortified with HHO. Each soil sample was assayed three times, with and without added water, and with and without HHO fortification. It was determined that water in soil up to 30% had no detectable effect on the method. These data are shown in Table 8.

9.4 The effect of the pH of the soil extract was determined by adjusting the soil pH of three soil samples. Soil samples were adjusted to pH 2 - 4 using 6N HCl and pH 10 - 12 using 6N NaOH. Aliquots of the pH adjusted soil samples were fortified with home heating oil. Each soil sample was assayed unadjusted and with pH adjusted to 2-4 and 10-12, both unfortified and fortified. These extracts were assayed three times. It was determined that soil samples with pH ranging from 2 to 12 had no detectable effect on the performance of the method. These data are shown in Table 9.

9.5 Two field studies were conducted at contaminated sites using the PETRO RISc Soil Test, EnSys, Inc.. In Field Trial 1, the method was used to locate soil contamination resulting from a leaking above ground gasoline tank. In Field Trial 2, the method was used to evaluate diesel fuel contamination in a railroad contaminated soil, sludge, and wastewater impound. Overall, a high degree of correlation was observed between the standard method and the immunoassay method. The application of the immunoassay method to 23 samples (46 analyses) resulted in eight conclusive false positive results (17%) and three conclusive false negative results (7%). Tables 10 and 11 summarize these results. There was agreement for 76% of the samples tested in the two trials for which data are presented.

9.6 Two field trials were undertaken to investigate the ability of the EnviroGard Petroleum Fuels in Soil Test Kit to identify soil samples which were contaminated with TPH. In trial 1 the method was used to identify soil which was contaminated with gasoline from leaking underground storage tanks. The immunoassay was compared to Method 8015. Twenty samples were analyzed by both methods. Interpreting the results at a cutoff of 100 ppm resulted in 1/20 (5%) false negatives and 0/20 (0%) false positives. In trial 2, the method was used to identify soil which was contaminated with JP-4 jet fuel from leaking semi-submerged storage tanks. The immunoassay was compared to Method 8015. Ten samples were analyzed by both methods. Interpreting the results at 1,000 ppm resulted in 0/10 (0%) false negatives and 1/10 (10%) false positives. Overall, for both field trials, there were 1/30 (3.3%) false negatives and 1/30 (3.3%) false positives. These data are summarized in Table 12.

10.0 REFERENCES

1. PETRO RISc™ Users Guide, Ensys Inc.

2. Marsden, P.J., S-F Tsang, and N. Chau, "Evaluation of the PETRO RISc™ kit Immunoassay Screen Test System", Science Applications International Corporation under contract to EnSys Inc., June 1992, unpublished

3. EnviroGard™ Petroleum Fuels in Soil Test Kit Guide, Millipore, Inc.

TABLE 1A

CROSS REACTIVITY[a]

Compound	Soil Equivalent Concentration (ppm) Required to Yield a Positive Result
Gasoline	100
Diesel fuel, regular #2	75
Jet A fuel	75
Kerosene	100
Fuel oil #2	100
Mineral Spirits	<30
Light lubricating oil	7,000
Lithium grease	10,000
Brake fluid	>10,000
Chain lubricant	>10,000
Toluene	200
o-Xylene	50
m-Xylene	100
p-Xylene	300
Ethylbenzene	50
Hexachlorobenzene	<30
Trichloroethylene	1,000
Acenaphthene	<30
Naphthalene	<30
Creosote	<30
2-Methylpentane	150
Hexanes, mixed	250
Heptane	300
iso-Octane	30
Undecane	>10,000

[a] PETRO RISc™ Soil Test, EnSys, Inc.

TABLE 1B

CROSS REACTIVITY[a]

Compound	Concentration Required for Positive Interpretation (ppm)
1,2,4 - Trimethylbenzene	0.1
m - Xylene	0.3
Acenaphthylene	0.3
Acenapthene	0.4
p - Xylene	0.5
Naphthalene	0.7
1,3,5 - Trimethylbenzene	2
Fluorene	2
Phenanthrene	2
o - Xylene	3
Ethylbenzene	5
Toluene	7
Propylbenzene	11
Chlordane	45
Benzene	70
Toxaphene	70

The following compounds were tested and found to yield negative results for concentrations up to 1000 ppm:

PCB (Aroclor 1248)	TNT
Pentachlorophenol	DDT

[a] EnviroGard™ Petroleum Fuels in Soil, Millipore, Inc.

TABLE 2

RESULTS FOR JP-4
(5 replicates/test)

Nominal concentration[a]	20 ppm	40 ppm	90 ppm	260 ppm	1000 ppm
PETRO RISc™ [b]	2/5, >40 ppm	5/5, >40 ppm	5/5, >40 ppm	1/5, >400 ppm	5/5, >400 ppm
Method 8015[c]	27 ± 2.1 ppm	38 ± 12 ppm	93 ± 30 ppm	260 ± 100 ppm	3000 ± 600 ppm
IR[d]	NA	2.8-5.3 ppm	52-95 ppm	380-620 ppm (1 outlier)	1370-2700 ppm

a. Samples were taken as cores at a contaminated Air Force Base. Nominal concentrations were determined by GC/FID analysis.

b. PETRO RISc™ test was run according to Method 4030 using the hydrocarbon supplied with the kit.

c. Method 8015 was run using a JP-4 standard, 20 ppm extract was not analyzed.

d. Method 418.1 was run using the mixture of solvents specified in the method. Because of the variability of the results, the range of values is reported. No analyses were conducted on the 20 ppm sample.

TABLE 3

RESULTS FOR LOW AROMATIC DIESEL
(5 replicates/test)

Nominal concentration[a]	12.5 ppm	75 ppm	105 ppm	150 ppm	1000 ppm
PETRO RISc™ [b]	4/4, <150 ppm	4/4, <150 ppm	5/5, <150 ppm	3/5, >150 ppm	5/5, >1500 ppm
Method 8015[c]	nd	54 ± 7 ppm	90 ± 15 ppm	125 ± 12 ppm	960 ± 105 ppm
IR[d]	30.5 -51.7 ppm	106.0 - 292.0 ppm	129.0 - 305.0 ppm	NA	810.0 - 1798.0 ppm

a. Samples were prepared by spiking sandy loam soil with known amounts of low aromatic diesel sold in California (Section 2256, CCR)

b. PETRO RISc™ test was run according to Method 4030 using the hydrocarbon supplied with the kit, 1/5 determinations at 35 and 75 ppm out of QC limits.

c. Method 8015 was run using a diesel standard purchased at a California station. nd - not detected.

d. Method 418.1 was run using the mixture of solvents specified in the method. Because of the variability of the results, the range of results is reported. NA - no IR determination made for the 150 ppm sample.

TABLE 4

RESULTS FOR REGULAR DIESEL
(4 replicates/test)

Nominal concentration[a]	25 ppm	75 ppm	150 ppm
PETRO RISc™ [b]	2/4, <75 ppm	2/3, >75 ppm	4/4, >75 ppm
Method 8015[c]	51.2 ± 6.4 ppm	75.9 ± 7.8 ppm	162 ± 10.4 ppm

a. Samples were prepared by spiking sandy loam soil with known amounts of regular number 2 diesel.

b. PETRO RISc™ test was run according to Method 4030 using the hydrocarbon supplied with the kit, one determination on 75 ppm sample out of QC limits.

c. Method 8015 was run using a diesel standard purchased at a Virginia station.

TABLE 5

RESULTS FOR OXYGENATED GASOLINE - FRESH SPIKE
(5 replicates/test)

Nominal concentration[a]	50 ppm	100 ppm	200 ppm	1000 ppm
PETRO RISc™ [b]	3/4, <100 ppm	4/5, >100 ppm	5/5, >100 ppm	5/5, >1000 ppm
Method 8015[c]	22.2 ± 1.6 ppm	39.4 ± 4.2 ppm	84.8 ± 10.9 ppm	434 ± 26 ppm

a. Samples were prepared by spiking sandy loam soil with known amounts of an oxygenated fuel, sample were maintained in closed jars until analyzed.

b. PETRO RISc™ test was run according to Method 4030 using the hydrocarbon supplied with the kit, one determination on 50 ppm sample out of QC limits.

c. Method 8015 was run using a gasoline standard purchased at a California station.

TABLE 6

RESULTS FOR OXYGENATED GASOLINE - HELD OPEN
(5 replicates/test)

Nominal concentration[a]	50 ppm	100 ppm	200 ppm
PETRO RISc™ [b]	3/4, <100 ppm	4/5, >100 ppm	2/4, >100 ppm
Method 8015[c]	nd	3.6 ± 0.4 ppm	7.3 ± 0.9 ppm

[a] Samples were prepared by spiking sandy loam soil with known amounts of an oxygenated fuel, analyses were conducted 24 hours after homogenizing the sample. Spiked samples were stored open to the atmosphere. Nominal concentrations are based on the spiking level.

[b] PETRO RISc™ test was run according to Method 4030 using the hydrocarbon supplied with the kit, 1/5 determinations at 50 and 200 ppm out of QC limits.

[c] Method 8015 was run using a gasoline standard purchased at a California station. Later eluting peaks were used for quantitation.

nd - not detected

TABLE 7

METHOD SENSITIVITY

Part 1 - Average Response with Negative Soils

Soil#	Soil Type	Average % Bo (n = 9)	Standard Deviation
SAND	91.4	4.1	
S2	LOAM	83.1	3.2
S3	CLAY	84.4	3.1
S4	LOAM	80.9	1.3
S5	CLAY	89.7	1.7
S6	LOAM/SAND	91.2	0.2
S7	SAND/LOAM	89.0	0.3
S8	LOAM	90.0	1.4
AVERAGE		87.5	4.0

Part 2 - Average Response with Calibrators

Calibrator Concentration (ppm)	Average Absorbance	Average %Bo
0	1.339	N/A
5	1.097	81.9
15	0.825	61.7
50	0.427	31.9
125	0.219	16.3

Part 3 - Method Sensitivity

Based on Part 1 and Part 2 Above:

Average %Bo - 2 SD = 79.6 which is equivalent to 5.8 ppm
Average %Bo - 3 SD = 75.6 which is equivalent to 7.0 ppm

(%Bo = [(OD_{sample}/$OD_{negative\ control}$)x100])

TABLE 8

EFFECT OF WATER CONTENT IN SOIL SAMPLES

Soil	% Water	Fortified?	Rep. 1*	Rep. 2	Rep. 3	Mean	Std. Dev.	± 2 SD Range
S1	0	No	101.3	99.1	111.8	104.1	6.8	90.4 - 117.7
S1	30	No	100.5	115.5	109.1	108.4	7.5	93.4 - 123.4
S1	0	Yes	59.2	65.8	69.6	64.9	5.3	49.9 - 75.5
S1	30	Yes	60	74.7	83.1	72.3	11.7	49.2 - 96.0
S2	0	No	57.9	53.9	72.3	61.4	9.7	42.0 - 80.8
S2	30	No	74.5	91.8	85.2	83.8	8.7	66.4 - 101.2
S2	0	Yes	40.3	40.9	45.6	42.3	2.9	36.5 - 48.1
S2	30	Yes	44.5	67.8	68.4	60.2	13.6	33.0 - 87.4
S3	0	No	70.1	85.6	76.7	77.5	7.8	61.9 - 93.1
S3	30	No	81.5	109.4	103.4	98.1	14.7	68.7 - 127.5
S3	0	Yes	41.1	46.6	60.7	49.5	10.1	29.3 - 69.7
S3	30	Yes	61.3	76.7	63.1	67.0	8.4	50.2 - 83.8

* All values shown are $\%Bo = [(OD_{sample}/OD_{negative\ control})x100]$

TABLE 9

EFFECT OF pH ON SOIL SAMPLES

Soil	pH Adj.	Fortified?	Rep.1*	Rep.2	Rep.3	Mean	Std. Dev.	± 2 SD Range
S1	None	No	88.9	93.2	92.8	91.6	2.4	86.8 - 96.4
S1	Acidic	No	108.9	66.0	88.1	87.7	21.5	44.7- 109.2
S1	Basic	No	101.2	90.3	90.6	94.0	6.2	81.6 - 106.4
S1	None	Yes	64.3	55.7	58.0	59.3	4.5	50.3 - 68.3
S1	Acidic	Yes	52.9	41.1	49.4	47.8	6.1	35.6 - 60.0
S1	Basic	Yes	69.3	61.7	57.5	62.8	6.0	50.8 - 74.8
S2	None	No	76.2	86.4	83.1	81.9	5.2	71.5 - 92.3
S2	Acidic	No	101.2	82.4	99.5	94.4	10.4	73.6 - 115.2
S2	Basic	No	89.9	72.1	77.7	79.9	9.1	61.7 - 98.1
S2	None	Yes	59.4	60.3	53.7	57.8	3.6	50.6 - 65.0
S2	Acidic	Yes	68.1	62.3	59.3	63.2	4.5	54.2 - 72.2
S2	Basic	Yes	47.8	51.7	39.4	46.3	6.3	33.7 - 58.9
S3	None	No	83.4	88.4	85.3	85.7	2.5	80.7 - 90.7
S3	Acidic	No	89.3	84.9	91.0	88.4	3.1	82.2 - 94.6
S3	Basic	No	80.6	84.2	90.3	85.0	4.9	75.2 - 94.8
S3	None	Yes	60.2	53.6	58.8	57.5	3.5	47.7 - 64.5
S3	Acidic	Yes	58.8	58.5	62.0	59.8	1.9	56.0 - 63.6
S3	Basic	Yes	53.4	41.8	59.9	51.7	9.2	33.3 - 70.1

* All values shown are $\%Bo = [(OD_{sample}/OD_{negative\ control})x100]$

TABLE 10

PETRO RISc™ SOIL TEST
FIELD TRIAL 1

Sample ID	IR Method (ppm)	100 ppm Test		1000 ppm Test	
		Result	Agreement Y, FP, FN	Result	Agreement Y, FP, FN
AST-01	<20	< 100	Y	< 1000	Y
AST-02	520	≥ 100	Y	≥ 1000	FP
AST-03	1700	≥ 100	Y	≥ 1000	Y
AST-04	130	≥ 100	Y	< 1000	Y
AST-05	20	≥ 100	FP	< 1000	Y
AST-06	40	≥ 100	FP	< 1000	FN
AST-07	400	≥ 100	Y	< 1000	FN
AST-08	640	≥ 100	Y	< 1000	FN
AST-09	1600	≥ 100	Y	≥ 1000	Y

Y = Immunoassay and GC or IR results agree
FP = False Positive
FN = False Negative

TABLE 11

PETRO RISc™ SOIL TEST
FIELD TRIAL 2

Sample ID	GC Extractables (ppm)	TRPH (ppm)	75 ppm Test			750 ppm Test		
			Result	Agreement Y, FP, FN		Result	Agreement Y, FP, FN	
				TRPH	GC		TRPH	GC
1-B	5720	20800	≥ 75	Y	Y	≥ 750	Y	Y
2-A	610	14700	≥ 75	Y	Y	≥ 750	FP	Y
2-B	370	6800	≥ 75	Y	Y	≥ 750	FP	Y
2-C	2270	1950	≥ 75	Y	Y	≥ 750	Y	Y
3-B	4870	18600	≥ 75	Y	Y	≥ 750	Y	Y
3-C	760	1180	≥ 75	Y	Y	< 750	FN*	FN
4-A	66	4100	≥ 75	FP*	Y	< 750	Y	FN
4-B	303	2100	≥ 75	Y	Y	< 750	Y	FN
5-A	20400	29600	≥ 75	Y	Y	≥ 750	Y	Y
5-B	26300	28600	≥ 75	Y	Y	≥ 750	Y	Y
5-C	267	330	≥ 75	Y	Y	≥ 750	FP	FP
6-B	550	22700	≥ 75	Y	Y	≥ 750	FP	Y
8	59300	64400	≥ 75	Y	Y	≥ 750	Y	Y
9	26500	12900	≥ 75	Y	Y	≥ 750	Y	Y

Y = Immunoassay and GC or IR results agree
FN = False Negative
FP = False Positive
FN* = False Negative, but within 25% of GC or IR results
FP* = False Positive, but within 25% of GC or IR results

TABLE 12

IMMUNOASSAY COMPARED TO METHOD 8015

Field Trial 1: Gasoline (Interpretation at 100 ppm)

Sample ID	Method 8015 (ppm)	Immunoassay	Concurrence?
MW-18-1	270	Negative	False Negative
MW-18-2	15	Negative	YES
MW-18-3	15	Negative	YES
MW-18-A1	20	Negative	YES
MW-18-A1 Duplicate	15	Negative	YES
MW-18-A2	1500	Positive	YES
DB3	300	Positive	YES
MW-12-3	250	Positive	YES
MW-13-1	40	Negative	YES
MW-13-3	50	Negative	YES
MW-13-4	20	Negative	YES
MW-17-3	250	Positive	YES
MW-17-4	180	Positive	YES
MW-17-5	180	Positive	YES
MW-16-2	11,500	Positive	YES
MW-16-2 Duplicate	11,500	Positive	YES
MW-19-2	10	Negative	YES
MW-19-3	70	Negative	YES
MW-14-1	280	Positive	YES
MW-17-A1	560	Positive	YES

Field Trial 2: JP-4 Jet Fuel (Interpretation at 1,000 ppm)

Sample ID	Method 8015 (ppm)	Immunoassay	Concurrence?
TB1 6.5-7.0	15,900	Positive	YES
TB2 6.5-7.0	16,800	Positive	YES
TB1 5.0-5.5	900	Negative	YES
TB2 5.0-5.5	100	Positive	False Positive
TB3 5.0-5.5	ND(<5)	Negative	YES
TB3 6.5-7.0	29,500	Positive	YES
TB5 5.0-5.5	5,000	Positive	YES
TB5 6.5-7.0	2,000	Positive	YES
TB4 6.5-7.0	19,000	Positive	YES
TB4 5.5-6.0	5,900	Positive	YES

METHOD 4035

SOIL SCREENING FOR POLYNUCLEAR AROMATIC HYDROCARBONS BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4035 is a procedure for screening soils to determine when total polynuclear aromatic hydrocarbons (PAHs) are present at concentrations above 1 mg/kg. Method 4035 provides an estimate for the concentration of PAHs by comparison with a PAH standard.

1.2 Using the test kit from which this method was developed, $\geq$95% of samples confirmed to have concentrations of PAHs below detection limits will produce a negative result in the 1 ppm test configuration.

1.3 The sensitivity of the test is influenced by the binding of the target analyte to the antibodies used in the kit. The commercial PAH kit used for evaluation of this method is most sensitive to the three (i.e., phenanthrene, anthracene, fluorene) and four (i.e., benzo(a)anthracene, chrysene, fluoranthene, pyrene) ring PAH compounds listed in Method 8310, and also recognizes most of the five and six ring compounds listed.

1.4 The sensitivity of the test is influenced by the nature of the PAH contamination and any degradation processes operating at a site. Although the action level of the test may vary from site to site, the test should produce internally consistent results at any given site.

1.5 In cases where the exact concentration of PAHs are required, quantitative techniques (i.e., Methods 8310, 8270, or 8100) should be used).

1.6 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 An accurately weighed sample is first extracted and the extract filtered using a commercially available test kit. The sample extract and an enzyme conjugate reagent are added to immobilized antibody. The enzyme conjugate "competes" with the PAHs present in the sample for binding to the immobilized anti-PAH antibody. The test is interpreted by comparing the response produced by testing a sample to the response produced by testing standard(s) simultaneously.

2.2 A portion of all samples in each analytical batch should be confirmed using quantitative techniques.

3.0 INTERFERENCES

3.1 Chemically similar compounds and compounds which might be expected to be found in conjunction with PAH contamination were tested to determine the concentration required to produce a positive result. These data are shown in Tables 1 and 2.

3.2 The kit was optimized to respond to three and four ring PAHs. The sensitivity of the test to individual PAHs is highly variable. Naphthalene, dibenzo(a,h)anthracene, and

benzo(g,h,i)perylene have 0.5 percent or less than the reactivity of phenanthrene with the enzyme conjugate.

3.3 The alkyl-substituted PAHs, chlorinated aromatic compounds, and other aromatic hydrocarbons, such as dibenzofuran, have been demonstrated to be cross-reactive with the immobilized anti-PAH antibody. The presence of these compounds in the sample may contribute to false positives.

4.0 APPARATUS AND MATERIALS

PAH RISc™ Soil Test (EnSys, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Soil samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

7.1 Method 4035 is intended for field or laboratory use.

7.2 Follow the manufacturer's instructions for the test being used. Those test kits used must meet or exceed the performance indicated in Tables 3-7.

7.3 The action limit for each application must be within the operating range of the kit used.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other kits.

8.5 Use the test kits within the specified storage temperature and operating temperature limits.

9.0 METHOD PERFORMANCE

9.1 The extraction efficiency of a commercially available test kit was tested (PAH RISc™ Test, EnSys Inc.) by spiking phenanthrene, benzo(a)anthracene and benzo(a)pyrene into PAH negative soil matrices (PAH-116 and PAH-141 are field samples). The soils were spiked using detection limits established for each compound (see Table 1), extracted and determined by immunoassay. The results for these 3-, 4- and 5-ring PAHs (Table 4) demonstrated that they were extracted with good recovery and yielded the correct assay interpretation.

9.2 A single laboratory study was conducted with a commercially available test kit (PAH RISc™ Test, EnSys Inc.), using 25 contaminated soil samples. Four replicate determinations were made on each test sample and the data compared with values obtained using HPLC Method 8310. Several analysts performed the immunoassay analyses. The immunoassay data agreed in all cases with the external HPLC data obtained (Table 5).

9.3 An additional single laboratory validation study on 30 randomly selected, PAH-contaminated field samples from multiple sites was run by the USEPA Region X Laboratory. Results are reported in Table 6 on an as found basis, and reported in Table 7 normalized to phenanthrene, based on cross-reactivity data (from Table 1). The false positive rate at the 1 ppm action level was 13% for unnormalized results and 19% for normalized results based on 31 analyses. The false negative rate at 1 ppm was 0 in both cases. At the 10 ppm action level, the false positive rate was 19% unnormalized and 26% normalized. False negative rates at 10 ppm were 6% unnormalized and 3% normalized.

9.4 The probabilities of generating false positive and false negative results at an action level of 1 ppm are listed in Table 3.

10.0 REFERENCES

1. PAH-RISc™ Users Guide, EnSys Inc.

2. P. P. McDonald, R. E. Almond, J. P. Mapes, and S. B. Friedman, "PAH-RISc™ Soil Test - A Rapid, On-Site Screening Test for Polynuclear Aromatic Hydrocarbons in Soil", J. of AOAC International (accepted for publication document #92263)

3. R. P. Swift, J. R. Leavell, and C. W. Brandenburg, "Evaluation of the EnSys PAH-RISc™ Test Kit", Proceedings, USEPA Ninth Annual Waste Testing and Quality Assurance Symposium, 1993.

TABLE 1

Cross-reactivity of Method 8310 PAHs

Compound	Concentration Giving a Positive Result (ppm Soil Equivalent)	Percent Cross-Reactivity
2 Rings		
Naphthalene	200	0.5
3 Rings		
Acenaphthene	8.1	12
Acenaphthylene	7.5	13
Phenanthrene	**1.0**	**100**
Anthracene	0.81	123
Fluorene	1.5	67
4 Rings		
Benzo(a)anthracene	1.6	64
Chrysene	1.2	84
Fluoranthene	1.4	73
Pyrene	3.5	29
5 Rings		
Benzo(b)fluoranthene	4.6	22
Benzo(k)fluoranthene	9.4	11
Benzo(a)pyrene	8.3	12
Dibenzo(a,h)anthracene	>200	<0.5
6 Rings		
Indeno(1,2,3-c,d)pyrene	11	9.4
Benzo(g,h,i)perylene	>200	<0.5

TABLE 2

Cross Reactivity of Other PAHs and Related Compounds

Compound	Concentration Giving a Positive Result (ppm, Soil Equivalent)	Percent Cross-Reactivity
Other PAHs		
1-Methylnaphthylene	54	1.8
2-Methylnaphthylene	58	1.7
1-Chloronaphthylene	59	1.7
Halowax 1013	18	5.7
Halowax 1051	>200	<0.5
Dibenzofuran	14	7.2
Other Compounds		
Benzene	>200	<0.5
Toluene	>200	<0.5
CCA	>200	<0.5
Phenol	>200	<0.5
Creosote	5.4	18.5
2,4,6-Trichlorobenzene	>200	<0.5
2,3,5,6-Tetrachlorobenzene	>200	<0.5
Pentachlorobenzene	>200	<0.5
Pentachlorophenol	>200	<0.5
Bis(2-ethylhexyl) phthalate	>200	<0.5
Aroclor 1254	>200	<0.5
Aroclor 1260	>200	<0.5

TABLE 3

Probability of False Negative and False Positive Results
for PAHs at A 1 ppm Action Level

Spike Concentration Phenanthrene (ppm)	Probability of False Positive (Mean ± SD)	Probability of False Negative (Mean ± SD)
0	0% ± 0%	N/A
0.4	23% ± 17%	N/A
0.8	94% ± 13%	N/A
1.0	N/A	0% ± 0%

Results were obtained from spiking four different validation lots, using 3 operators, 12 matrices for a total of 201 determinations at each concentration of phenanthrene.

N/A = No false positive or negative possible above action limit.

TABLE 4

Spike Recovery of Phenanthrene, Benzo(a)anthracene and Benzo(a)pyrene

Compound	Spike (ppm)	Soil	PAH RISc™ Results
Blank	0	Wake	<1
Blank	0	PAH-116	<1
Phenanthrene	1	Wake	1-10
Phenanthrene	1	PAH-116	1-10
Phenanthrene	1	PAH-141	1-10
Phenanthrene	10	Wake	>10
Phenanthrene	10	PAH-116	>10
Phenanthrene	10	PAH-141	>10
Benzo(a)anthracene	1.6	Wake	1-10
Benzo(a)anthracene	1.6	PAH-116	1-10
Benzo(a)anthracene	16	Wake	>10
Benzo(a)anthracene	16	PAH-116	>10
Benzo(a)pyrene	8.3	Wake	1-10
Benzo(a)pyrene	8.3	PAH-116	1-10
Benzo(a)pyrene	83	PAH-116	>10

TABLE 5

Powerplant Field Samples (Soil) Evaluated by Immunoassay

Field Sample Number	EnSys Method Immunoassay (ppm)	Method 8310 HPLC (ppm)
PAH-137	>10	<21
PAH-141	<1	<21
PAH-118	1-10	<26
PAH-136	>10	26
PAH-139	>10	<28
PAH-126	1-10, >10	<32
PAH-127	>10	<33
PAH-122	>10	<33
PAH-138	>10	33
PAH-131	>10	<34
PAH-128	>10	<35
PAH-132	>10	<43
PAH-112	>10	<48
PAH-140	>10	50
PAH-130	>10	54
PAH-116	<1	<61
PAH-135	>10	71
PAH-133	>10	<91
PAH-119	>10	<100
PAH-120	>10	<161
PAH-124	>10	<167
PAH-134	>10	182
PAH-114	>10	<247
PAH-113	>10	<294
PAH-115	>10	<343

TABLE 6

Total PAH Content of Region X Field Samples Using EnSys
PAH RISc™ Immunoassay Test Kit

Sample ID	1 ppm Test		10 ppm Test		GC/MS Lab Result (ppm)[1]	False +/-	
	<1	>1	<10	>10		Eval @ 1 ppm	Eval @ 10 ppm
PAH-1		*		*	0.2	+	+
PAH-2				*	12.2		
PAH-3				*	16.0		
PAH-4	*				0.00		
PAH-5	*				0.5		
PAH-6		*		*	8.7		+
PAH-7				*	148		
PAH-8				*	182		
PAH-9		*		*	4.4		+
PAH-10		*		*	0.2	+	+
PAH-11	*				0.00		
PAH-12				*	85.4		
PAH-12Dup				*	85.4		
PAH-13				*	28.5		
PAH-14	*		*		0.3		
PAH-15		*			0.6	+	
PAH-16	*		*		0.00		
PAH-17		*		*	1.8		+
PAH-18		*	*		3.4		
PAH-19		*	*		6.7		
PAH-20	*		*		0.9		
PAH-21				*	43.2		

[1] Sum of all PAHs detected.

TABLE 6 (cont.)

Sample ID	1 ppm Test		10 ppm Test		GC/MS Lab Result (ppm)[1]	False +/-	
	<1	>1	<10	>10		Eval @ 1 ppm	Eval @ 10 ppm
PAH-22				*	72.8		
PAH-23		*		*	1.3		+
PAH-24		*	*		0.3	+	
PAH-25	*		*		0.4		
PAH-26			*		27.9		-
PAH-27	*		*		0.00		
PAH-28			*		16.4		-
PAH-29	*		*		0.4		
PAH-30		*	*		9.6		

TABLE 7

Total PAH Content of Region X Field Samples Using EnSys
PAH RISc™ Immunoassay Test Kit Normalized to Cross-reactivity

Sample ID	1 ppm Test		10 ppm Test		GC/MS Lab Result (ppm)[1]	False +/-	
	<1	>1	<10	>10		Eval @ 1 ppm	Eval @ 10 ppm
PAH-1		*		*	0.1	+	+
PAH-2				*	8.1		+
PAH-3				*	9.0		+
PAH-4	*				0.00		
PAH-5	*				0.2		
PAH-6		*		*	5.2		+
PAH-7				*	56.9		
PAH-8				*	73.2		

[1] Sum o f all PAHs detected.

TABLE 7 (cont.)

Sample ID	1 ppm Test		10 ppm Test		GC/MS Lab Result (ppm) [1]	False +/-	
	<1	>1	<10	>10		Eval @ 1 ppm	Eval @ 10 ppm
PAH-9		*		*	0.1	+	+
PAH-10		*		*	0.00	+	+
PAH-11	*				0.00		
PAH-12				*	47.3		
PAH-12Dup				*	47.3		
PAH-13				*	11.5		
PAH-14	*		*		0.2		
PAH-15		*			0.5	+	
PAH-16	*		*		0.00		
PAH-17		*		*	1.2		+
PAH-18		*	*		1.7		
PAH-19		*	*		3.6		
PAH-20	*		*		0.6		
PAH-21				*	27.5		
PAH-22				*	49.2		
PAH-23		*		*	0.8	+	+
PAH-24		*	*		0.1	+	
PAH-25	*		*		0.2		
PAH-26			*		13.5		-
PAH-27	*		*		0.00		
PAH-28			*		6.4		
PAH-29	*		*		0.2		
PAH-30		*	*		2.8		

[1] Sum of all PAHs detected.

METHOD 4040

SOIL SCREENING FOR TOXAPHENE BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4040 is a procedure for screening soils to determine whether toxaphene (CAS Registry 8001-35-2) is present at concentrations above 0.5 µg/g. Method 4040 provides an estimate for the concentration of toxaphene by comparison against standards.

1.2 In cases where the exact concentration of toxaphene is required, additional techniques (i.e., gas chromatography (Method 8081) or gas chromatography/mass spectrometry (Method 8270)) should be used.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed.

2.2 In general, the method is performed using an extract of a soil sample. Filtered extracts may be stored cold, in the dark. An aliquot of the extract and an enzyme-toxaphene conjugate reagent are added to an immobilized toxaphene antibody. The enzyme-toxaphene conjugate "competes" with toxaphene present in the sample for binding to the immobilized toxaphene antibody. The enzyme-toxaphene conjugate bound to the toxaphene antibody then catalyzes a colorless substrate to a colored product. The test is interpreted by comparing the color produced by a sample to the response produced by a reference reaction.

3.0 INTERFERENCES

3.1 Compounds that are chemically similar may cause a positive test (false positive) for toxaphene. The test kit used to develop this method was evaluated for interferences, and found to be relatively insensitive to other organochlorine pesticides (e.g., Lindane, DDT and DDE). The data for the lower limit of detection of these compounds are provided in Table 1. Consult the information provided by the manufacturer of the kit used for additional information regarding cross reactivity with other compounds.

3.2 Storage and use temperatures may modify the method performance. Follow the manufacturer's directions for storage and use.

4.0 APPARATUS AND MATERIALS

Immunoassay test kit: EnviroGard™ Toxaphene in Soil (Millipore, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Soils samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

Follow the manufacturer's instructions for the test kit being used.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other test kits.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4040 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

Table 2 provides the results of single determinations in soil from New Mexico.

10.0 REFERENCES

1. EnviroGard™ Toxaphene Soil Test Kit Guide, Millipore, Inc.

2. Marsden, P.J., S-F Tsang, V. Frank, N. Chau, and M. Roby, "Comparison of the Millipore Immunoassay for Toxaphene with Soxhlet Extraction and Method 8081", Science Applications International Corporation, under contract to Millipore Inc., May 1994, unpublished.

TABLE 1

POSSIBLE SOIL INTERFERENCES (a)

Compound	Soil Equivalent Concentration µg/kg (ppb) Required to Yield a Positive Result
Diesel fuel	45000
Endrin	6
Endosulfan I	6
Endosulfan II	6
Dieldrin	6
Heptachlor	6
Aldrin	20
Technical Chlordane	14
gamma-BHC (Lindane)	300
alpha-BHC	1000
delta-BHC	1000

The following compounds were found to yield a negative result for concentrations up to 200,000 µg/kg:

Gasoline
Pentachlorophenol
DDT
PCB (Aroclor 1248)
Trinitrotoluene

(a) Millipore, Inc. product literature

TABLE 2

TOXAPHENE (µg/g) RESULTS FOR NEW MEXICO SOIL SAMPLES

Method 3540/8081 (Lab 1)	Method 4040 (Lab 2)	AGREEMENT
0.09 J	<0.5	Y
0.04 J	>0.5	FP
0.04 J	>0.5	FP
0.01 J	<0.5	Y
40	>0.5	Y
19.3	>0.5	Y
<0.50	<0.5	Y
<0.50	>0.5	FP
0.26 J	>0.5	FP
1.0	>0.5	Y
0.14 J	>0.5	FP
0.27 J	>0.5	FP
27.2	>0.5	Y
0.14 J	>0.5	FP
0.48 J	>0.5	Y
0.21 J	>0.5	FP
6.0	NA	-
6.0	NA	-
4.8	>0.5	Y
0.049 J	>0.5	FP
0.054 J	>0.5	FP
1.3	>0.5	Y
0.15 J	>0.5	Y
0.058 J	>0.5	FP
89.6	>0.5	Y
0.5	>0.5	Y

TABLE 2 (cont.)

Method 3540/8081 (Lab 1)	Method 4040 (Lab 2)	AGREEMENT
3.7	NA	-
3.6	NA	-
35.6	>0.5	Y
0.16 J	>0.5	FP
0.88	>0.5	Y
0.41 J	>0.5	FP
0.30 J	>0.5	FP
0.10 J	>0.5	FP
323	>0.5	Y

NA = not analyzed
J = an estimate value. This is used to indicate the result is less than the sample quantitation limit but greater than zero.
Y = Yes, FN = False Negative, FP = False Positive

METHOD 4041

SOIL SCREENING FOR CHLORDANE BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4041 is a procedure for screening soils to determine whether chlordane (CAS Registry 57-74-9) is present at concentrations above 20, 100 or 600 µg/kg. Method 4041 provides an estimate for the concentration of chlordane by comparison against standards.

1.2 In cases where the exact concentration of chlordane is required, additional techniques [i.e., gas chromatography (Method 8081) or gas chromatography/mass spectrometry (Method 8270)] should be used.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed.

2.2 In general, the method is performed using an extract of a soil sample. Filtered extracts may be stored cold, in the dark. An aliquot of the extract and an enzyme-chlordane conjugate reagent are added to immobilized chlordane antibody. The enzyme-chlordane conjugate "competes" with chlordane present in the sample for binding to chlordane antibody. The enzyme-chlordane conjugate bound to the chlordane antibody then catalyzes a colorless substrate to a colored product. The test is interpreted by comparing the color produced by a sample to the response produced by a reference reaction.

3.0 INTERFERENCES

3.1 Compounds that are chemically similar may cause a positive test (false positive) for chlordane. The test kit used to develop this method was evaluated for interferences. The data for the lower limit of detection of these compounds are provided in Table 1. Consult the information provided by the manufacturer of the kit used for additional information regarding cross reactivity with other compounds.

3.2 Storage and use temperatures may modify the method performance. Follow the manufacturer's directions for storage and use.

4.0 APPARATUS AND MATERIALS

4.1 Immunoassay test kit: EnviroGard™ Chlordane in Soil (Millipore, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Soil samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance specifications indicated in Tables 2-5.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Method 4000 and Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other test kits.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4041 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 Method sensitivity was determined by establishing the "noise" level expected from matrix effects encountered in negative soil samples and determining the corresponding Chlordane concentration by comparison to the analyte-specific response curve. 8 different soils which did not contain Chlordane were assayed. Each of these soils was extracted in triplicate and each extract was assayed in three different assays. The mean and the standard deviation of the resulting %Bo's ($\%Bo = [(OD_{sample}/OD_{negative\ control})x100]$) was calculated and the sensitivity was estimated at two standard deviations below the mean. The sensitivity for Method 4041 was determined to be 80% Bo at a 95% confidence interval. Based on the average assay response to Chlordane, this corresponds to 6.4 µg/kg Chlordane. These data are shown in Table 2.

9.2 The effect of water content of the soil samples was determined by assaying three different soil samples which had been dried and subsequently had water added to 30% (w/w). Aliquots of these samples were then fortified with Chlordane (100 µg/kg). Each soil sample was assayed three times, with and without added water, and with and without Chlordane fortification. It was determined that water in soil up to 30% had no detectable effect on the method. These data are shown in Table 3.

9.3 The effect of the pH of the soil extract was determined by adjusting the soil pH of three soil samples. Soil samples were adjusted to pH 2 - 4 using 6N HCl and pH 10 - 12 using 6N NaOH. Aliquots of the pH adjusted soil samples were fortified with Chlordane (100 µg/kg). Each soil sample was assayed unadjusted and with pH adjusted to 2-4 and 10-12, both unfortified and fortified. It was determined that soil samples with pH ranging from 3 to 11 had no detectable effect on the performance of the method. These data are shown in Table 4.

9.4 A field trial was undertaken to evaluate to ability of the EnviroGard™ Chlordane in Soil Test Kit to identify chlordane contaminated soil at a remediation site. A total of 32 soil samples were evaluated by both Method 4041 and Method 8080. Interpretation of the results at a 1 mg/kg cutoff resulted in 2/32 (6.3%) false negatives and 0/32 (0%) false positives. Interpretation of the results at a cutoff of 10 mg/kg resulted in 0/32 (0%) false negatives and 2/32 (6.3%) false positives. These data are shown in Table 5.

10.0 REFERENCES

1. EnviroGard™ Chlordane in Soil Test Kit Guide, Millipore, Inc.

TABLE 1

CROSS REACTIVITY

Compound	Concentration Required for Positive Interpretation (µg/kg)
Chlordane	5
Endrin	3
Endosulfan I	3
Endosulfan II	3
Dieldrin	3
Heptachlor	3
Aldrin	10
Toxaphene	100
gamma-BHC (Lindane)	300
alpha-BHC	1000
delta-BHC	1000
The following compounds were found to yield a negative result for concentrations up to 200,000 µg/kg: Gasoline Pentachlorophenol PCB (Aroclor 1248) Trinitrotoluene	

TABLE 2

METHOD SENSITIVITY

Part 1 - Average Response with Negative Soils

Soil No.	Soil Type	Average %Bo (n = 8)	Standard Deviation
S1	Loam/sand	92.8	2.0
S2	Loam	86.2	1.0
S3	Clay	85.5	8.8
S4	Clay	95.4	1.1
S5	Clay	83.9	2.6
S6	Loam/sand	88.5	1.8
S7	Sand	81.4	2.7
S8	Sand	95.8	0.8
AVERAGE		88.7	4.5

Part 2 - Average Response with Chlordane Calibrators

Chlordane Concentration (µg/kg)	Average Absorbance	Average %Bo
0	1.043	N/A
5	0.882	84.4
25	0.598	57.2
125	0.322	30.8
500	0.159	15.2

Part 3 - Method Sensitivity

Based on Part 1 and Part 2 Above:

Average %Bo - 2 SD = 79.7 which is equivalent to 6.4 µg/kg Chlordane

Average %Bo - 3 SD = 75.2 which is equivalent to 8.6 µg/kg Chlordane

TABLE 3

EFFECT OF WATER CONTENT IN SOIL SAMPLES

Soil	% Water	Fortified?	Rep. 1	Rep. 2	Rep. 3	Mean	Std. Dev.	± 2 SD Range
S1	0	No	95.2	101	94.5	97.0	3.7	89.6 - 104
S1	30	No	96.0	99.2	96.0	97.1	1.8	93.5 - 101
S1	0	Yes	40.5	38.5	35.9	38.3	2.3	33.7 - 42.9
S1	30	Yes	42.2	43.0	43.0	42.8	0.5	41.8 - 43.8
S2	0	No	85.8	87.1	85.5	86.1	0.9	84.3 - 87.9
S2	30	No	78.7	84.9	79.8	81.1	3.3	74.5 - 87.8
S2	0	Yes	37.7	39.5	40.6	39.3	1.5	36.3 - 42.3
S2	30	Yes	39.8	38.8	37.0	38.5	1.4	35.7 - 41.3
S3	0	No	76.6	76.6	73.0	75.4	2.1	71.2 - 79.6
S3	30	No	87.4	88.7	85.7	87.3	1.5	84.3 - 90.3
S3	0	Yes	40.0	40.2	35.7	38.7	2.5	33.7 - 43.7
S3	30	Yes	40.8	37.1	38.7	38.9	1.9	35.1 - 42.7

TABLE 4

EFFECT OF pH OF SOIL SAMPLES

Soil	pH Adj.	Fortified?	Rep. 1*	Rep. 2	Rep. 3	Mean	Std. Dev.	± 2 SD Range
S1	None	No	97.5	87.8	94.8	93.4	5.0	83.4 - 103
S1	Acidic	No	97.4	114	94.7	102	10.7	80.8 - 124
S1	Basic	No	107	114	93.8	105	10.1	84.7 - 125
S1	None	Yes	43.6	47.5	38.5	43.2	4.5	34.2 - 52.2
S1	Acidic	Yes	43.6	51.8	34.1	43.2	8.8	25.6 - 60.8
S1	Basic	Yes	44.8	50.8	32.0	42.5	9.6	23.3 - 61.7
S2	None	No	87.8	86.3	87.6	87.3	0.8	85.7 - 88.9
S2	Acidic	No	94.2	108	80.5	94.1	13.5	67.1 - 121
S2	Basic	No	89.3	99.3	77.9	88.8	10.7	67.4 - 110
S2	None	Yes	43.9	48.9	33.9	42.2	7.7	26.8 - 57.6
S2	Acidic	Yes	44.6	55.9	41.5	47.4	7.6	32.2 - 62.6
S2	Basic	Yes	42.3	59.2	36.5	46.0	11.8	22.4 - 69.6
S3	None	No	72.3	74.5	79.3	75.4	3.6	68.2 - 82.6
S3	Acidic	No	85.3	105	75.7	88.8	15.1	58.6 - 119
S3	Basic	No	89.4	83.8	85.9	86.4	2.8	80.8 - 92.0
S3	None	Yes	44.5	49.5	32.6	42.2	8.7	24.8 - 59.6
S3	Acidic	Yes	40.5	52.1	34.7	42.4	8.9	24.6 - 60.2
S3	Basic	Yes	40.6	37.1	43.9	40.5	3.4	33.7 - 47.3

* All values shown are $\%Bo = [(OD_{sample}/OD_{negative\ control})x100]$

TABLE 5

CORRELATION TO METHOD 8081

Test Interpretation at 1 mg/kg

Sample ID	Method 8081 (mg/kg)	Immunoassay (mg/kg)	Results Agree?
co-ss-2	45	POSITIVE	YES
co-ss-3	4.9	POSITIVE	YES
co-ss-4	25	POSITIVE	YES
co-ss-5	1.4	NEGATIVE	FALSE NEGATIVE
co-ss-6	2.7	POSITIVE	YES
co-ss-7	2.5	POSITIVE	YES
co-ss-8	<1.0	NEGATIVE	YES
co-ss-9	7.9	POSITIVE	YES
co-ss-10	6.0	POSITIVE	YES
co-ss-13	5.2	POSITIVE	YES
co-ss-14	2.9	POSITIVE	YES
co-ss-15	2.1	POSITIVE	YES
co-ss-17	<1.0	NEGATIVE	YES
co-ss-20	2.8	NEGATIVE	FALSE NEGATIVE
co-ss-21	<1.0	NEGATIVE	YES
co-ss-22	<1.0	NEGATIVE	YES
co-ss-23	<1.0	NEGATIVE	YES
co-ss-24	51	POSITIVE	YES
co-ss-25	1.4	POSITIVE	YES
co-ss-26	<1.0	NEGATIVE	YES
co-ss-27	<1.0	NEGATIVE	YES
co-ss-28	9.6	POSITIVE	YES
co-ss-28-17D	2.6	POSITIVE	YES
co-ss-29	14	POSITIVE	YES
co-ss-30	1.8	POSITIVE	YES
co-ss-31	<1.0	NEGATIVE	YES
co-ss-32	<1.0	NEGATIVE	YES
co-ss-33	2.9	POSITIVE	YES
co-ss-34	4.2	POSITIVE	YES
co-ss-35	<1.0	NEGATIVE	YES
co-ss-36	5.9	POSITIVE	YES
co-ss-41	<1.0	NEGATIVE	YES

TABLE 5 (cont.)

Test Interpretation at 10 mg/kg

Sample ID	Method 8081 (mg/kg)	Immunoassay (mg/kg)	Results Agree?
co-ss-2	45	POSITIVE	YES
co-ss-3	4.9	NEGATIVE	YES
co-ss-4	25	POSITIVE	YES
co-ss-5	1.4	NEGATIVE	YES
co-ss-6	2.7	NEGATIVE	YES
co-ss-7	2.5	NEGATIVE	YES
co-ss-8	<1.0	NEGATIVE	YES
co-ss-9	7.9	POSITIVE	FALSE POSITIVE
co-ss-10	6.0	POSITIVE	FALSE POSITIVE
co-ss-13	5.2	NEGATIVE	YES
co-ss-14	2.9	NEGATIVE	YES
co-ss-15	2.1	NEGATIVE	YES
co-ss-17	<1.0	NEGATIVE	YES
co-ss-20	2.8	NEGATIVE	YES
co-ss-21	<1.0	NEGATIVE	YES
co-ss-22	<1.0	NEGATIVE	YES
co-ss-23	<1.0	NEGATIVE	YES
co-ss-24	51	POSITIVE	YES
co-ss-25	1.4	NEGATIVE	YES
co-ss-26	<1.0	NEGATIVE	YES
co-ss-27	<1.0	NEGATIVE	YES
co-ss-28	9.6	NEGATIVE	YES
co-ss-28-17D	2.6	NEGATIVE	YES
co-ss-29	14	POSITIVE	YES
co-ss-30	1.8	NEGATIVE	YES
co-ss-31	<1.0	NEGATIVE	YES
co-ss-32	<1.0	NEGATIVE	YES
co-ss-33	2.9	NEGATIVE	YES
co-ss-34	4.2	NEGATIVE	YES
co-ss-35	<1.0	NEGATIVE	YES
co-ss-36	5.9	NEGATIVE	YES
co-ss-41	<1.0	NEGATIVE	YES

METHOD 4042

SOIL SCREENING FOR DDT BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4042 is a procedure for screening soils to determine whether 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane (DDT) (CAS Registry 50-29-3) and its breakdown products (DDD, DDE, and DDA) are present at concentrations above 0.2, 1.0 or 10 mg/kg. Method 4042 provides an estimate for the sum of concentrations of DDT and daughter compounds by comparison against standards.

1.2 In cases where the exact concentration of DDT is required, additional techniques [i.e., gas chromatography (Method 8081) or gas chromatography/mass spectrometry (Method 8270)] should be used.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed.

2.2 In general, the method is performed using an extract of a soil sample. Filtered extracts may be stored cold, in the dark. An aliquot of the extract and an enzyme-DDT conjugate reagent are added to immobilized DDT antibody. The enzyme-DDT conjugate "competes" with DDT present in the sample for binding to DDT antibody. The enzyme-DDT conjugate bound to the DDT antibody then catalyzes a colorless substrate to a colored product. The test is interpreted by comparing the color produced by a sample to the response produced by a reference reaction.

3.0 INTERFERENCES

3.1 Compounds that are chemically similar may cause a positive test (false positive) for DDT. The test kit used to develop this method was evaluated for interferences. The data for the lower limit of detection of these compounds are provided in Table 1. Consult the information provided by the manufacturer of the kit used for additional information regarding cross reactivity with other compounds.

3.2 Storage and use temperatures may modify the method performance. Follow the manufacturer's directions for storage and use.

4.0 APPARATUS AND MATERIALS

4.1 Immunoassay test kit: EnviroGard™ DDT in Soil (Millipore, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Soil samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance specifications indicated in Tables 2-5.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Method 4000 and Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other test kits.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4042 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 Method sensitivity was determined by establishing the "noise" level expected from matrix effects encountered in negative soil samples and determining the corresponding DDT concentration by comparison to the analyte-specific response curve. Eight different soils which did not contain DDT were assayed. Each of these soils was extracted in triplicate and each extract was assayed in three different assays. The mean and the standard deviation of the resulting %Bo's (%Bo = $[(OD_{sample}/OD_{negative\ control})x100]$) were calculated and the sensitivity was estimated at two standard deviations below the mean. The sensitivity for Method 4042 was determined to be 81.4% Bo at a 95% confidence inteval. Based on the average assay response to DDT, this corresponds to 0.044 ppm DDT. These data are shown in Table 2.

9.2 The effect of water content of the soil samples was determined by assaying three different soil samples which had been dried and subsequently had water added to 30% (w/w). Aliquots of these samples were then fortified with DDT (1.0 mg/kg). Each soil sample was assayed three times, with and without added water, and with and without DDT fortification. It was determined that water in soil up to 30% had no detectable effect on the method. These data are shown in Table 3.

9.3 The effect of the pH of the soil extract was determined by adjusting the soil pH of three soil samples. Soil samples were adjusted to pH 2 - 4 using 6N HCl and pH 10 - 12 using 6N NaOH. Aliquots of the pH adjusted soil samples were fortified with DDT (1.0 mg/kg). Each soil sample was assayed unadjusted and with pH adjusted to 2-4 and 10-12, both unfortified and fortified. It was determined that soil samples with pH ranging from 3 to 11 had no detectable effect on the performance of the method. These data are shown in Table 4.

9.4 A field study was conducted at a contaminated site using a commercially available test kit (EnviroGard™ DDT in Soil Test Kit, Millipore Corp.). The immunoassay was used to identify soil which had been contaminated with DDT. The standard method (Method 8081) was performed at a certified laboratory and the results were compared to the immunoassay. When interpreting the results at a 0.2 ppm cutoff, the immunoassay yielded 0/32 (0%) false negatives and 2/32 (6.3%) false positives. When interpreting the results at a 1.0 ppm cutoff, the immunoassay yielded 1/32 (3.1%) false negatives and 2/32 (6.3%) false positives. These data are shown in Table 5.

10.0 REFERENCES

1. EnviroGard™ DDT in Soil Test Kit Guide, Millipore, Inc.

TABLE 1

CROSS REACTIVITY

Compound	Concentration Required for Positive Interpretation (ppm)
p,p'-DDT	0.04
p,p'-DDD	0.01
p,p'-DDE	0.18
o,p'-DDT	4.0
o,p'-DDD	0.4
o,p'-DDE	3.0
DDA	0.002
Chloropropylate	0.007
Chlorobenzilate	0.03
Dicofol	0.14
Chloroxuron	24
Monolinuron	25
Thiobencarb	5
Tebuconazole	7
Neburon	17
Tetradifon	1.2
Diclofop	70
PCB (Aroclor 1248)	90

The following analytes are not detected at or above 100 ppm:

2,4-D	4-Chlorophenoxyacetic acid	Chlordane
Pentachlorophenol	Chlorbromuron	Chlortoluron
Dicamba	Diflubenzuron	Diuron
Lindane	Linuron	MCPA acid
MCPB	Mecoprop	Gasoline
Diesel fuel	2,4,6-Trinitrotoluene	Toxaphene

TABLE 2

METHOD SENSITIVITY

Part 1 - Average Response with Negative Soils

Soil No.	Soil Type	Average %Bo (n = 9)	Standard Deviation
S1	Loam	87.0	7.5
S2	Clay	93.2	2.3
S3	Sand	97.2	2.6
S4	Loam	87.7	1.2
S5	Loam/sand	88.1	2.3
S6	Clay	100.8	2.1
S7	Loam/sand	103.6	0.3
S8	Sand/loam	89.6	4.5
AVERAGE		93.4	6.0

Part 2 - Average Response with DDT Calibrators

DDT Concentration (ppm)	Average Absorbance	Average %Bo
0	1.133	N/A
0.1	0.897	79.4
1.0	0.569	50.3
10.0	0.362	32.0
50.0	0.259	22.9

Part 3 - Method Sensitivity

Based on Part 1 and Part 2 Above:

Average %Bo - 2 SD = 81.4 which is equivalent to 0.044 ppm DDT

Average %Bo - 3 SD = 75.4 which is equivalent to 0.097 ppm DDT

TABLE 3

EFFECT OF WATER CONTENT IN SOIL SAMPLES

Soil	% Water	Fortified?	Rep. 1	Rep. 2	Rep. 3	Mean	Std. Dev.	± 2 SD Range
S1	0	No	79.7*	79.3	83.7	80.9	2.4	76.1 - 85.7
S1	30	No	89.1	84.0	85.9	86.4	2.6	81.2 - 91.6
S1	0	Yes	49.8	62.1	46.3	52.8	8.3	36.2 - 69.4
S1	30	Yes	55.8	59.9	58.0	57.9	2.1	53.7 - 62.1
S2	0	No	85.2	96.2	97.9	93.1	6.9	79.3 - 106.9
S2	30	No	94.8	94.3	95.0	94.7	0.3	94.1 - 95.3
S2	0	Yes	54.4	47.0	56.1	52.5	4.8	42.9 - 62.1
S2	30	Yes	56.3	53.8	60.2	56.8	3.2	50.4 - 63.2
S3	0	No	96.2	91.3	100.0	95.8	4.3	87.2 - 104.4
S3	30	No	95.6	90.5	96.4	94.2	3.2	87.8 - 100.6
S3	0	Yes	54.8	52.9	54.8	54.2	1.1	52.0 - 56.4
S3	30	Yes	59.4	55.0	54.5	56.3	2.7	50.9 - 61.7

* All values shown are $\%Bo = [(OD_{sample}/OD_{negative\ control})x100]$

TABLE 4

EFFECT OF pH OF SOIL SAMPLES

Soil	pH Adj.	Fortified?	Rep. 1*	Rep. 2	Rep. 3	Mean	Std. Dev.	± 2 SD Range
S1	None	No	91.4	91.3	78.3	87.0	7.5	72.0 - 102
S1	Acidic	No	79.7	87.0	86.8	84.5	4.1	76.3 - 92.7
S1	Basic	No	80.5	84.5	78.5	81.2	3.0	75.2 - 87.2
S1	None	Yes	57.5	60.3	55.1	57.6	2.6	52.4 - 62.8
S1	Acidic	Yes	54.2	60.6	55.2	56.7	3.4	49.9 - 63.5
S1	Basic	Yes	52.8	60.2	53.3	55.5	4.1	47.3 - 63.7
S2	None	No	94.7	90.6	94.5	93.2	2.3	88.6 - 97.8
S2	Acidic	No	87.8	100.1	100.9	96.3	7.3	81.7 - 111
S2	Basic	No	87.9	81.6	98.3	89.3	8.5	72.3 - 106
S2	None	Yes	51.7	56.9	48.3	52.3	4.3	43.7 - 60.9
S2	Acidic	Yes	52.2	61.0	55.2	56.1	4.5	47.1 - 65.1
S2	Basic	Yes	52.0	53.5	48.9	51.5	2.3	46.9 - 56.1
S3	None	No	99.1	94.2	98.2	97.2	2.6	92.0 - 102
S3	Acidic	No	86.4	84.3	85.5	85.4	1.1	83.2 - 87.6
S3	Basic	No	94.9	100.3	92.9	96.1	3.8	88.5 - 104
S3	None	Yes	56.2	54.3	52.8	54.4	1.7	51.0 - 57.8
S3	Acidic	Yes	54.5	53.5	53.9	54.0	0.5	53.0 - 55.0
S3	Basic	Yes	54.6	57.2	62.9	58.2	4.2	49.8 - 66.6

* All values shown are $\%Bo = [(OD_{sample}/OD_{negative\ control})x100]$

TABLE 5

COMPARISON TO METHOD 8081

Test Interpretation at 0.2 mg/kg

Sample ID	Method 8081 (mg/kg)	Immunoassay (mg/kg)	Results Agree?
co-ss-2	3.6	POSITIVE	YES
co-ss-3	0.55	POSITIVE	YES
co-ss-4	2.3	POSITIVE	YES
co-ss-5	<0.05	NEGATIVE	YES
co-ss-6	0.15	POSITIVE	FALSE POSITIVE
co-ss-7	0.3	POSITIVE	YES
co-ss-8	0.1	NEGATIVE	YES
co-ss-9	0.8	POSITIVE	YES
co-ss-10	0.23	POSITIVE	YES
co-ss-13	0.79	POSITIVE	YES
co-ss-14	0.58	POSITIVE	YES
co-ss-15	0.35	POSITIVE	YES
co-ss-17	<0.05	NEGATIVE	YES
co-ss-20	0.18	NEGATIVE	YES
co-ss-21	0.06	NEGATIVE	YES
co-ss-22	<0.05	NEGATIVE	YES
co-ss-23	<0.05	NEGATIVE	YES
co-ss-24	1.2	POSITIVE	YES
co-ss-25	0.12	NEGATIVE	YES
co-ss-26	<0.05	NEGATIVE	YES
co-ss-27	<0.05	NEGATIVE	YES
co-ss-28	0.16	NEGATIVE	YES
co-ss-28-17D	0.18	POSITIVE	FALSE POSITIVE
co-ss-29	0.69	POSITIVE	YES
co-ss-30	0.73	POSITIVE	YES
co-ss-31	0.68	POSITIVE	YES
co-ss-32	<0.05	NEGATIVE	YES
co-ss-33	0.32	POSITIVE	YES
co-ss-34	0.23	POSITIVE	YES
co-ss-35	0.52	POSITIVE	YES
co-ss-36	1.0	POSITIVE	YES
co-ss-41	<0.05	NEGATIVE	YES

Test Interpretation at 1.0 mg/kg

Sample ID	Method 8081 (mg/kg)	Immunoassay (mg/kg)	Results Agree?
co-ss-2	3.6	POSITIVE	YES
co-ss-3	0.55	NEGATIVE	YES
co-ss-4	2.3	POSITIVE	YES
co-ss-5	<0.05	NEGATIVE	YES
co-ss-6	0.15	NEGATIVE	YES
co-ss-7	0.3	NEGATIVE	YES
co-ss-8	0.1	NEGATIVE	YES
co-ss-9	0.8	NEGATIVE	YES
co-ss-10	0.23	NEGATIVE	YES
co-ss-13	0.79	NEGATIVE	YES
co-ss-14	0.58	NEGATIVE	YES
co-ss-15	0.35	NEGATIVE	YES
co-ss-17	<0.05	NEGATIVE	YES
co-ss-20	0.18	NEGATIVE	YES
co-ss-21	0.06	NEGATIVE	YES
co-ss-22	<0.05	NEGATIVE	YES
co-ss-23	<0.05	NEGATIVE	YES
co-ss-24	1.2	POSITIVE	YES
co-ss-25	0.12	NEGATIVE	YES
co-ss-26	<0.05	NEGATIVE	YES
co-ss-27	<0.05	NEGATIVE	YES
co-ss-28	0.16	NEGATIVE	YES
co-ss-28-17D	0.18	NEGATIVE	YES
co-ss-29	0.69	NEGATIVE	YES
co-ss-30	0.73	POSITIVE	FALSE POSITIVE
co-ss-31	0.68	POSITIVE	FALSE POSITIVE
co-ss-32	<0.05	NEGATIVE	YES
co-ss-33	0.32	NEGATIVE	YES
co-ss-34	0.23	NEGATIVE	YES
co-ss-35	0.52	NEGATIVE	YES
co-ss-36	1.0	NEGATIVE	FALSE NEGATIVE
co-ss-41	<0.05	NEGATIVE	YES

METHOD 4050

TNT EXPLOSIVES IN SOIL BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4050 is a procedure for screening soil samples to determine when trinitrotoluene (TNT, CAS No. 118-96-7) is present at concentrations above 0.5 mg/kg. Method 4050 provides an estimate for the concentration of TNT by comparison with a reference.

1.2 Using the test kit from which this method was developed, 93% of soil samples containing 0.25 ppm or less of TNT will produce a negative result, and 99+% of soil samples containing 1.0 ppm or greater of TNT will produce a positive result.

1.3 In cases where the exact concentrations of TNT are required, quantitative techniques (i.e., Method 8330) should be used.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed.

2.2 In general, the method is performed using an extract of a soil sample. Samples and an enzyme-TNT conjugate reagent are added to a immobilized TNT antibody. The enzyme-TNT conjugate "competes" with TNT present in the sample for binding to the immobilized TNT antibody. The enzyme-TNT conjugate bound to the TNT antibody then catalyzes a colorless substrate to a colored product. The test is interpreted by comparing the color produced by a sample to the response produced by a reference reaction.

3.0 INTERFERENCES

Chemically similar compounds and compounds that might be expected to be found in conjunction with TNT contamination were tested to determine the concentration required to produce a positive test result. Table 1 provides the concentrations of compounds tested with the D TECH™ test kit that are required to elicit a positive response at the MDL, as well as the concentration required to yield 50% inhibition compared to the standard curve.

4.0 APPARATUS AND MATERIALS

Immunoassay test kit: D TECH™ TNT (Strategic Diagnostics Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND TRANSPORTATION

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Soil samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance specifications indicated in Tables 3-6.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other test kits. Do not mix reagents from one kit lot with a different kit lot.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4050 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides data on the minimum concentrations of possible interferants and co-contaminants required to elicit a positive response in the test kits evaluated.

9.2 Twenty five soil samples, known to not be contaminated with TNT, were extracted and analyzed using the D TECH™ TNT kit to determine the extent of soil matrix effects on the performance of the test kit. The results are provided in Table 2, and show that false positive results are not attributable to soil components.

9.3 Thirty soil samples, known to not be contaminated with TNT, were each spiked with TNT at one-half and two times the MDL (0.25 and 1.0 ppm respectively). These samples were analyzed with the D TECH™ TNT test kit to determine the error rate of the assay. The results are presented in Table 3 .

9.4 Ten different soil types, all known to not be contaminated with TNT, were spiked with an acetone solution containing approximately 1.0 ppm TNT. This spiking solution was later quantitated by Method 8330 and found to contain 0.77 ppm TNT. The spiked soil samples were analyzed three (3) times with the D TECH™ kit to determine the extraction efficiency of the method. The data are presented in Table 4.

9.5 Table 5 presents the results of analysis of three soils spiked at approximately 1 and 3 ppm TNT. Each sample was analyzed once using Method 8330 and ten times using the D TECH™ kit.

9.6 Tables 6A and 6B present the results of two field trials. In each trial, soil samples were obtained at a West Coast site from borings, using a split spoon technique. The samples were homogenized by placing approximately six cubic inches of soil into a stainless steel vessel and mixing for five minutes with a stainless steel trowel. The soil was aliquotted into two (2) six ounce glass bottles, tested on-site using the D TECH™ method and transported to commercial laboratories (one laboratory per field trial) for analysis by Method 8330. Table 6C presents the results of a third party field trial, conducted by the California Department of Health Services.

10.0 REFERENCES

1. D TECH™ TNT Users Guide , SDI/EM Sciences 1994

2. Hutter,L., G. Teaney, and J.W.Stave, "A Novel Field Screening System for TNT Using EIA", in Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Vol 1, Proceedings of the 1993 U.S. EPA/A&WMA International Symposium, p.472, 1993.

3. Teaney, G., J.Melby, L.Hutter and J.Stave, "A Novel Field Analytical Method for TNT", Proceedings of the American Association of Analytical Chemists, 1993.

4. Haas, R.J., and B.P. Simmons, "Measurement of Trinitrotoluene (TNT) and Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in Soil by Enzyme Immunoassay and High Performance Liquid Chromatography (EPA Method 8330)", California Environmental Protection Agency, Department of Toxic Substances Control, Hazardous Materials Laboratory, March, 1995.

TABLE 1

CROSS REACTANTS
D TECH™ TNT TEST KIT

COMPOUND	MDL[a] (ppm)	IC 50[b] (ppm)	% CROSS REACTIVITY[c]
TNT (2,4,6-trinitrotoluene)	0.5	17	100
Tetryl[d]	3	48	35
1,3,5-trinitrobenzene	4	75	23
2-amino-4,6-dinitrotoluene	13	150	11
4-amino-2,6-dinitrotoluene	>500	>500	<1
2,4-dinitrotoluene	90	390	4
2,6-diaminonitrotoluene	>500	>500	<1
2-nitrophenol	>500	>500	<1
4-nitrophenol	>500	>500	<1
2,4-dinitrophenol	>500	>500	<1
RDX[d]	>500	>500	<1
HMX[d]	>500	>500	<1

The following compounds were not detected at or above 100 ppm:

Benzene	Xylenes	PCB 1254	Triazine
Ethylbenzene	Toluene	PCP	

PAHs - an equal concentration mixture of:

Acenaphthene	Acenaphthalene	Anthracene
1,2-Benzanthracene	Benzo(a)pyrene	Pyrene
Benzo(b)fluoranthene	Chrysene	Phenanthrene
Benzo(ghi)perylene	Fluoranthene	Fluorene
Benzo(k)fluoranthene	Indeno(123-cd)pyrene	Naphthalene
Dibenz(ah)anthracene		

[a] The Method Detection Limit (MDL) is defined as the lowest concentration of compound that yields a positive test result.

[b] The IC_{50} is defined as the concentration of compound required to produce a test response equivalent to 50% of the maximum response.

[c] % Cross reactivity is determined by dividing the equivalent TNT concentration by the actual compound concentration at IC_{50}

[d] Tetryl = methyl-2,4,6-trinitrophenylnitramine
RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine
HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

TABLE 2

SOIL MATRIX EFFECTS

Soil	Soil type		D TECH™ RANGE (ppm)
133	Avonburg Fine Sine Silt	N/A	<0.5
101	Matapeake Silt Loam	DE	<0.5
100	Clay Loam	DE	<0.5
102	Sassafras Sand Loam	DE	<0.5
106	Evesboro Low Organic Sand	DE	<0.5
107	Pokomoke High OM Sand	DE	<0.5
109	Davidson Clay Loam	GA	<0.5
111	Shontic Casa Grande Sand	AZ	<0.5
112	Casa Grande Clay Loam	AZ	<0.5
113	Trix Sand Clay Loam	AZ	<0.5
114	Trix Casa Grande Clay Loam	AZ	<0.5
115	Yolo Loam	CA	<0.5
116	Capay Silt Clay	CA	<0.5
117	Sycamore Silt Loam	CA	<0.5
118	Dennis Silt Loam	KS	<0.5
119	Grundy Silt Clay Loam	KS	<0.5
120	Luray Silt Clay Loam	OH	<0.5
121	Wooster Silt Loam	OH	<0.5
122	Vienna Loam	SD	<0.5
123	Opal Clay	SD	<0.5
124	Raub Silt Loam	IN	<0.5
125	Rockfield Silt Loam	IN	<0.5
127	Cisne	IL	<0.5
128	Muscatine Loam	IL	<0.5
130	Sandy Brae	DE	<0.5

TABLE 3

FALSE NEGATIVE AND FALSE POSITIVE RATES, SOIL MATRIX[a]

Spike Concentration	False Positive Rate	False Negative Rate
0.25 ppm	7%	-
1.0 ppm	-	0%

[a] Thirty negative soils were spiked with TNT at one-half and two times the MDL (0.25 and 1.0 ppm respectively). These samples were analyzed with the D TECH™ TNT test kit to determine the error rate of the assay.

TABLE 4

DETERMINATION OF EXTRACTION EFFICIENCY FROM SOIL SAMPLES[a]

SOIL ID	MEAN TNT CONC. (ppm)	SD	%CV	%RECOVERY
101	0.54	0.04	7	70
106	0.64	0.06	9	84
108	0.87	0.18	20	113
109	0.63	0.08	13	82
110	0.88	0.15	17	115
116	1.02	0.15	17	115
117	0.82	0.15	15	132
123	0.87	0.23	26	113
126	0.95	0.26	28	123
128	0.65	0.11	16	84
SPIKING SOLUTION	0.77	N/A	N/A	100

[a] Ten different TNT negative soils were spiked with an acetone solution containing 0.77 TNT. The spiked soil samples were analyzed three times with the D TECH™ kit to determine the extraction efficiency of the method.

TABLE 5
RECOVERY OF TNT SPIKED INTO REAL SOILS

Three (3) soils were spiked at approximately 1 and 3 ppm TNT. Each sample was analyzed once by Method 8330 and ten (10) times by the D TECH™ TNT immunoassay test product.

SAMPLE ID	AMOUNT SPIKED	D TECH™ (ppm)	HPLC METHOD 8330	AGREEMENT Y, FN, FP
106-1	1.0	0.5 - 1.5	0.69	Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		1.5 - 3.0		FP
116-1	1.0	0.5 - 1.5	0.73	Y
		0.5 - 1.5		Y
		1.5 - 3.0		FP
		0.5 - 1.5		Y
		0.5 - 1.5		
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		1.5 - 3.0		FP
128-1	1.0	0.5 - 1.5	0.75	Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		1.5 - 3.0		FP
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y
		0.5 - 1.5		Y

TABLE 5 (cont.)

RECOVERY OF TNT SPIKED INTO REAL SOILS

SAMPLE ID	AMOUNT SPIKED	D TECH™ (ppm)	HPLC METHOD 8330	AGREEMENT[a] Y, FN, FP
106-3	3.0	1.5 - 3.0	1.53	Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		0.5 - 1.5		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		0.5 - 1.5		Y
116-3	3.0	1.5 - 3.0	2.12	Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		0.5 - 1.5		N
		1.5 - 3.0		Y
128-3	3.0	0.5 - 1.5	2.07	FN
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y
		1.5 - 3.0		Y

TABLE 6A

COMPARISON OF D TECH™ SOIL RESULTS WITH METHOD 8330

SAMPLE ID	D TECH™ RANGE (ppm)	METHOD 8330 TNT (ppm)	AGREEMENT[a] Y, FN, FP
61-1	< 0.2	< 0.09	Y
61-10	< 0.2	< 0.09	Y
61-11	< 0.2	< 0.09	Y
61-12	< 0.2	< 0.09	Y
61-13	< 0.2	< 0.09	Y
61-14	< 0.2	< 0.09	Y
61-15	< 0.2	< 0.09	Y
61-16	< 0.2	< 0.09	Y
61-17	< 0.2	< 0.09	Y
61-18	< 0.2	< 0.09	Y
61-19	< 0.2	< 0.09	Y
61-2	> 1.5	> 3.0	Y
61-20	< 0.2	< 0.09	Y
61-21	0.5-1.0	2.44	FN
61-22	< 0.2	< 0.09	Y
61-23	< 0.2	< 0.09	Y
61-24	1.0-1.5	1.4	Y
61-25	< 0.2	< 0.09	Y
61-26	< 0.2	< 0.09	Y
61-27	0.2-0.5	0.27	Y
61-28	< 0.2	< 0.09	Y
61-29	< 0.2	< 0.09	Y
61-3	1.0-1.5	1.3	Y
61-30	< 0.2	< 0.09	Y
61-4	> 1.5	1.1	FP
61-5	0.5 - 1.0	1.0	Y
61-6	> 1.5	> 3.0	Y
61-7	< 0.2	< 0.09	Y
61-8	0.5-1.0	1.0	Y
61-9	0.2-0.5	0.56	Y
TET-1	0.5-1.0	< 0.09	FP
TET-2	< 0.2	< 0.09	Y

TABLE 6A (cont.)

SAMPLE ID	D TECH™ RANGE (ppm)	METHOD 8330 TNT (ppm)	AGREEMENT[a] Y, FN, FP
TET-3	< 0.2	< 0.09	Y
TL-1	0.2-0.5	0.99	FN
TL-2	> 1.5	1.2	FP
TL-3	> 1.5	> 3.0	Y
TL-4	0.2-0.5	0.66	FN
TL-5	> 1.5	> 3.0	Y
TL-6	0.2-0.5	0.66	FN
TL-7	0.2-0.5	0.71	FN
TL-8	0.5-1.0	1.46	FN
TL-9	0.2-0.5	0.92	FN

Y = Yes, FN = False Negative, FP = False Positive

TABLE 6B

COMPARISON OF D TECH™ SOIL RESULTS WITH METHOD 8330

Sample Number	D TECH™ Range (ppm)	8330 TNT (ppm)	8330 TNB (ppm)	TNT Equivalent (ppm)	AGREEMENT Y, FN, FP
1	> 1.5	5.75	< 1.0	5.75-6.0	Y
2	> 1.5	3.32	< 1.0	3.32-3.57	Y
3	> 1.5	166	< 1.0	166	Y
4	> 1.5	2500	18.50	2504	Y
5	> 1.5	2.72	< 1.0	2.72-2.97	Y
6	> 1.5	<2.0	7.02	1.76-3.76	Y
7	> 1.5	<2.0	5.12	1.28-3.28	Y
8	> 1.5	140	12.2	143	Y
9	> 1.5	230	20.2	235	Y
10	> 1.5	1100	16.9	1104	Y
11	> 1.5	23.5	11.5	26.0	Y
12	0.5 - 1.0	<2.0	2.95	0.74-2.74	Y
13	0.5 - 1.0	<2.0	1.30	0.33-2.33	Y
14	0.5 - 1.0	<2.0	1.89	0.47-2.47	Y
15	> 1.5	<2.0	3.94	0.99-2.99	Y
16	0.5 - 1.0	<2.0	4.54	1.14-3.14	FN
17	> 1.5	<2.0	4.57	1.14-3.14	Y
18	> 1.5	<2.0	10.5	2.63-4.63	Y
19	> 1.5	3.23	24.3	9.3	Y
20	> 1.5	<2.0	81	20.3	Y
21	> 1.5	<2.0	1.61	0.40-2.40	Y
22	> 1.5	4.75	2.60	5.40	Y
23	> 1.5	<2.0	2.97	0.74-2.74	Y
24	> 1.5	<2.0	6.29	1.57-3.57	Y
25	> 1.5	<2.0	< 1.0	<2.25	Y
26	> 1.5	3.64	5.05	4.90	Y
27	> 1.5	<2.0	6.62	1.66-3.66	Y
28	> 1.5	<2.0	1.94	0.49-2.49	Y
29	> 1.5	<2.0	8.53	2.13-4.13	Y
30	> 1.5	<2.0	6.77	1.69-3.69	Y
31	> 1.5	<2.0	6.75	1.69-3.69	Y
32	> 1.5	<2.0	17.6	4.40-6.41	Y

TABLE 6B (cont.)

Sample Number	D TECH™ Range (ppm)	8330 TNT (ppm)	8330 TNB (ppm)	TNT Equivalent (ppm)	AGREEMENT Y, FN, FP
33	> 1.5	6.39	39.2	16.2	Y
34	> 1.5	4.20	1.39	4.55	Y
35	> 1.5	5.14	< 1.0	5.14-5.39	Y
36	> 1.5	<2.0	2.68	0.67-2.67	Y
37	> 1.5	<2.0	7.65	1.91-3.91	Y
38	> 1.5	<2.0	27.70	6.9-8.9	Y
39	> 1.5	<2.0	9.01	2.25-4.25	Y
40	> 1.5	<2.0	30.90	7.7-9.7	Y
41	> 1.5	<2.0	35.70	8.9-10.9	Y
42	> 1.5	820	5.69	821	Y
43	> 1.5	1200	24.0	1206	Y
44	> 1.5	27.6	11.9	31	Y
45	> 1.5	7.43	9.01	9.70	Y
46	> 1.5	4.98	9.46	7.40	Y
47	> 1.5	3.32	10.4	5.90	Y
48	> 1.5	3.42	16.5	7.60	Y
49	> 1.5	4.32	28.2	11.4	Y
50	> 1.5	7.57	44.8	18.8	Y
50	> 1.5	5.12	81.2	25.4	Y
51	> 1.5	<2.0	1.64	0.41-2.41	Y
52	0.5 - 1.0	<2.0	2.27	0.57-2.57	Y
53	> 1.5	33.5	23.4	39.4	Y
54	> 1.5	2.19	8.43	4.30	Y
55	> 1.5	7.00	11.0	9.75	Y
56	> 1.5	2.84	4.69	4.01	Y
57	> 1.5	<2.0	5.67	1.42-3.42	Y
58	> 1.5	2.23	12.8	5.43	Y
59	> 1.5	5.38	31.4	13.23	Y
60	> 1.5	2.60	13.0	5.85	Y
61	> 1.5	4.43	31.1	12.2	Y
62	> 1.5	4.79	25.9	11.3	Y
63	> 1.5	2.29	18.2	6.8	Y
64	1.0 - 1.5	8.84	148	45.8	FN
65	> 1.5	9.01	< 1.0	9.01	Y
66	> 1.5	29.00	6.02	30.50	Y

TABLE 6B (cont.)

Sample Number	D TECH™ Range (ppm)	8330 TNT (ppm)	8330 TNB (ppm)	TNT Equivalent (ppm)	AGREEMENT Y, FN, FP
67	> 1.5	<2.0	1.30	0.33-2.33	Y
78	> 1.5	<2.0	7.50	1.88-3.88	Y
69	> 1.5	<2.0	4.70	1.18-3.18	Y
70	> 1.5	2.49	30.0	9.99	Y
71	> 1.5	<2.0	29.1	7.28-9.28	Y
72	> 1.5	<2.0	8.86	2.22-4.22	Y
73	> 1.5	<2.0	30.7	7.68-9.68	Y
74	> 1.5	<2.0	38.1	9.59-11.6	Y
75	> 1.5	3.98	183	49.7	Y
76	> 1.5	5.67	122	36.2	Y
77	> 1.5	7.05	< 1.0	7.05-7.3	Y
78	> 1.5	8.04	< 1.0	8.04-8.29	Y
79	> 1.5	1000	7.49	1001	Y
80	0.5 - 1.0	2.12	2.99	2.87	FN
81	0.5 - 1.0	8.83	5.56	10.20	FN
82	1.0 - 1.5	3.64	3.20	4.44	FN
83	> 1.5	3.22	10.6	5.87	Y
84	> 1.5	<2.0	18.3	4.58-6.58	Y
85	> 1.5	<2.0	17.4	4.43-6.43	Y
86	> 1.5	<2.0	20.4	5.10-7.10	Y
87	> 1.5	<2.0	117	29.2-31.2	Y
88	1.0 - 1.5	<2.0	1.96	0.49-2.49	Y
89	> 1.5	351	5.77	352	Y
90	> 1.5	116	39.2	126	Y
91	> 1.5	4.29	3.92	5.27	Y
92	> 1.5	<2.0	11.6	2.9-4.9	Y
93	> 1.5	2.34	9.26	4.66	Y
94	> 1.5	<2.0	48.7	12.2-14.2	Y
95	0.5 - 1.0	<2.0	5.05	1.26-3.26	FN
95	> 1.5	<2.0	12.6	3.15-5.15	Y
96	> 1.5	<2.0	10.7	2.68-4.68	Y
97	> 1.5	<2.0	11.1	2.78-4.78	Y
98	> 1.5	<2.0	3.74	0.94-2.94	Y
99	< 0.2	<2.0	1.88	0.47-2.47	FN
100	> 1.5	4.24	< 1.0	4.24-4.49	Y

TABLE 6B (cont.)

Sample Number	D TECH™ Range (ppm)	8330 TNT (ppm)	8330 TNB (ppm)	TNT Equivalent (ppm)	AGREEMENT Y, FN, FP
101	> 1.5	<2.0	1.10	0.28-2.28	Y
102	0.5 - 1.0	<2.0	1.28	0.32-2.32	Y
103	1.0 - 1.5	<2.0	2.70	0.68-2.68	Y
104	> 1.5	<2.0	10.5	2.63-4.63	Y
105	> 1.5	<2.0	14.1	3.53-5.53	Y
106	> 1.5	<2.0	18.4	4.6-6.6	Y
107	0.5 - 1.0	<2.0	6.35	1.59-3.59	FN
108	1.0 - 1.5	<2.0	6.66	1.67-3.67	FN
109	0.5 - 1.0	<2.0	21.8	5.45-7.45	FN
110	0.5 - 1.0	<2.0	5.29	1.32-3.32	FN
111	0.5 - 1.0	<2.0	4.49	1.12-3.12	FN
112	1.0 - 1.5	<2.0	16.3	4.08-6.08	FN
113	> 1.5	<2.0	28.7	7.18-9.18	Y
114	> 1.5	<2.0	17.7	4.43-6.43	Y
115	> 1.5	<2.0	24.1	6.03-8.03	Y
116	0.2 - 0.5	6.35	< 1.0	6.35-6.6	FN
117	0.5 - 1.0	<2.0	2.40	0.60-2.6	Y
118	0.2 - 0.5	<2.0	4.70	1.18-3.18	FN
119	0.5 - 1.0	<2.0	11.6	2.9-4.9	FN
120	> 1.5	<2.0	56.9	14.2-16.2	Y
121	> 1.5	<2.0	45.6	11.4-13.4	Y
122	> 1.5	<2.0	67.7	16.9-18.9	Y
123	0.2 - 0.5	<2.0	2.78	0.7-2.7	FN
124	< 0.2	<2.0	1.61	0.4-2.4	FN
125	< 0.2	<2.0	4.07	1.02-3.02	FN
126	0.2 - 0.5	<2.0	3.12	0.78-2.78	FN
127 through 279	< 0.2	<2.0	<1.0	<2.25	Y
280 through 365	0.2 - 0.5	<2.0	< 1.0	<2.25	Y
366 through 381	0.5 - 1.0	<2.0	< 1.0	<2.25	Y

TABLE 6B (cont.)

Sample Number	D TECH™ Range (ppm)	8330 TNT (ppm)	8330 TNB (ppm)	TNT Equivalent (ppm)	AGREEMENT Y, FN, FP
382 through 391	1.0 - 1.5	<2.0	< 1.0	<2.25	Y
392 through 399	> 1.5	<2.0	< 1.0	<2.25	Y

Y = Yes, FN = False Negative, FP = False Positive

TABLE 6C

COMPARISON OF D TECH™ SOIL RESULTS WITH METHOD 8330
Third Party Field Trial

Sample	Dilution Factor	D TECH™ Results	8330 TNT Results	8330 TNT+TNB Results	AGREEMENT Y, FN, FP
1	1	<0.5	<0.15	<0.25	Y
2	1	<0.5	<0.15	<0.25	Y
3	1	<0.5	<0.15	<0.25	Y
4	1	0.5-1.5	<0.15	<0.25	FP
5	1	<0.5	<0.15	<0.25	Y
6	1	0.5-1.5	<0.15	<0.25	FP
7	1	<0.5	<0.15	<0.25	Y
8	1	<0.5	<0.15	<0.25	Y
9	1	<0.5	<0.15	<0.25	Y
10	1	<0.5	<0.15	<0.25	Y
11	1	<0.5	<0.15	<0.25	Y
12	1	<0.5	<0.15	<0.25	Y
13	1	<0.5	<0.15	<0.25	Y
14	1	<0.5	<0.15	<0.25	Y
15	1	<0.5	<0.15	<0.25	Y
16	1	0.5-1.5	<0.15	<0.25	FP
17	1	<0.5	<0.15	<0.25	Y
18	1	<0.5	<0.15	<0.25	Y
19	1	0.5-1.5	<0.15	<0.25	FP
20	1	<0.5	<0.15	<0.25	Y
21	1	<0.5	<0.15	<0.25	Y
22	1	<0.5	<0.15	<0.25	Y
23	1	<0.5	<0.15	<0.25	Y
24	1	0.5-1.5	<0.15	<0.25	FP

TABLE 6C (cont.)

Sample	Dilution Factor	D TECH™ Results	8330 TNT Results	8330 TNT+TNB Results	AGREEMENT Y, FN, FP
25	1	<0.5	<0.15	<0.25	Y
26	1	<0.5	<0.15	<0.25	Y
27	1	<0.5	<0.15	<0.25	Y
28	1	0.5-1.5	<0.15	<0.25	FP
29	1	<0.5	<0.15	<0.25	Y
30	1	0.5-1.5	0.15-0.99	0.15-0.99	Y
31	1	<0.5	<0.15	<0.25	Y
32	1	0.5-1.5	<0.15	<0.25	FP
33	1	0.5-1.5	<0.15	<0.25	FP
34	1	0.5-1.5	0.15-0.99	0.15-0.99	Y
35	1	<0.5	<0.15	<0.25	Y
36	1	<0.5	<0.15	<0.25	Y
37	1	3.0-4.0	0.15-0.99	0.25-2.0	FP
38	1	<0.5	<0.15	<0.25	Y
39	1	<0.5	<0.15	<0.25	Y
40	1	<0.5	<0.15	<0.25	Y
41	1	0.5-1.5	<0.15	<0.25	FP
42	1	1.5-3.0	0.15-0.99	0.15-0.99	FP
43	1	<0.5	<0.15	<0.25	Y
44	1	0.5-1.5	<0.15	0.15-0.99	Y
45	1	0.5-1.5	<0.15	<0.25	FP
46	1	0.5-1.5	<0.15	<0.25	FP
47	1	0.5-1.5	<0.15	1.3	Y
48	1	<0.5	<0.15	<0.25	Y
49	1	0.5-1.5	<0.15	<0.25	FP
50	1	<0.5	<0.15	<0.25	Y
51	1	0.5-1.5	<0.15	<0.25	FP
52	10	5-15	1.4	3.2	Y

TABLE 6C (cont.)

Sample	Dilution Factor	D TECH™ Results	8330 TNT Results	8330 TNT+TNB Results	AGREEMENT Y, FN, FP
53	10	40-50	35	41.67	Y
54	1	0.5-1.5	<0.15	<0.15	FP
55	1	0.5-1.5	0.15-0.99	0.15-0.99	Y
56	1	1.5	0.15-0.99	0.15-0.99	Y
57	1	0.5-1.5	<0.15	<0.15	FP
58	1	3.0-4.0	0.15-0.99	0.15-0.99	FP
59	1	0.5-1.5	<0.15	<0.15	FP
60	10	15-30	22	22.48	Y
61	1	0.5-1.5	-	<0.15	FP
62	10	4-40	2.1	32	Y
63	10	5-15	2	3.1	Y
64	100	400-500	360	364	Y
65	1000	4000-5000	6300	6327	Y
66	10000	15000	4000	4027	FP
67	1000	15000	530	547	FP
68	10	5-15	2.8	3.375	Y
69	100	400-500	460	477	Y
70	10	15-30	4.2	6.73	FP
71	10	5-15	1.0	1.57	FP
72	10	40	5.1	34.5	Y
73	10	5-15	1.9	4	Y
74	10	5	1.6	2.7	Y
75	10	4-30	2.2	4.3	Y
76	10	5-15	1.7	2	FP
77	10	5-15	2.2	3.95	Y
78	100	300-400	180	192.19	Y
79	10	5-15	3.1	4.61	Y
80	10	5-15	2.8	5.26	Y

TABLE 6C (cont.)

Sample	Dilution Factor	D TECH™ Results	8330 TNT Results	8330 TNT+TNB Results	AGREEMENT Y, FN, FP
81	10	5-15	2.5	5.26	Y
82	10	15-30	3.2	4.5	FP
83	10	40-50	1	23	Y
84	10	15-30	3.8	18.5	Y
85	10	15-30	36	52.5	FN
86	10	15-30	3.6	8.66	Y
87	10	5-15	2.6	19.16	Y
88	10	5-15	3.2	3.84	Y
89	100	150-300	78	82	Y
90	1	4-5	18000	18050	FN
91	10000	15000	11000	11052.9	Y
92	10	40-50	36	42.4	Y
93	10000	15000-30000	11000	11052.9	Y
94	1000	500-1500	88	107	FP
95	1	3.0	9.6	10.17	FN
96	10000	40000-50000	15000	15050	FP
97	10000	4000-5000	2200	2220	Y
98	10	15-30	3.6	3.9	FP
99	10	15-30	6.4	6.7	FP
100	100	50-150	26	28.76	Y

Y = Yes, FN = False Negative, FP = False Positive

HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE (RDX) IN SOIL BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4051 is a procedure for screening soils to determine when hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, CAS No. 121-82-4) is present at concentrations above 0.5 mg/kg Method 4051 provides an estimate of the concentration of RDX by comparison with a reference.

1.2 Using the test kit from which this method was developed, 99+% of soil samples containing 0.25 ppm or less of RDX will produce a negative result and 99+% of soil samples containing 1.0 ppm will produce a positive result.

1.3 In cases where the exact concentration of RDX is required, quantitative techniques (i.e., Method 8330) should be used.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

Test kits are commercially available for this method. The manufacturer's directions should be followed. In general, the method is performed using an extract of a soil sample. Samples and an enzyme conjugate reagent are added to immobilized RDX antibody. The enzyme-RDX conjugate "competes" with RDX present in the sample for binding to an immobilized RDX antibody. The enzyme-RDX conjugate bound to the antibody then catalyzes a colorless substrate to a colored product. The test is interpreted by comparing the color produced by a sample to the response produced by a reference reaction.

3.0 INTERFERENCES

Chemically similar compounds and compounds which might be expected to be found in conjunction with RDX contamination were tested to determine the concentration required to produce a positive test result. Table 1 provides the concentrations of compounds tested with the D TECH™ test kit that are required to elicit a positive response at the MDL, as well as the concentration required to yield 50% inhibition compared to the standard curve.

4.0 APPARATUS AND MATERIALS

Immunoassay test kit: D TECH™ RDX (Strategic Diagnostics Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HAULING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Soil samples may be contaminated, and should therefore be considered hazardous and handled accordingly.

7.0 PROCEDURE

Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance indicated in Tables 3-6.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other test kits. Do not mix reagents from one kit lot with a different kit lot.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4051 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides data on the minimum concentrations of possible interferants and co-contaminants required to elicit a positive response in the test kits evaluated.

9.2 Twenty six soil samples, known to not be contaminated with RDX, were extracted and analyzed using the D TECH™ RDX kit to determine the extent of soil matrix effects on the performance of the test kit. The results are provided in Table 2, and show that false positive results are not attributable to soil components.

9.3 Thirty soil samples, known to not be contaminated with RDX, were each spiked with RDX at one-half and two times the MDL (0.25 and 1.0 ppm respectively). These samples were analyzed with the D TECH™ RDX test kit to determine the error rate of the assay. The results are presented in Table 3.

9.4 Ten different soil types, all known not to be contaminated with RDX, were spiked with RDX. The spiked soil samples were each analyzed six times with the D TECH™ kit to determine the extraction efficiency of the method. The data are presented in Table 4.

9.5 Table 5 presents the results of analysis of three soils spiked at approximately 0.4, 1 and 3 ppm RDX. Each sample was analyzed using Method 8330 and in triplicate using the D TECH™ kit.

9.6 Tables 6A through 6D present the results of four field trials. Freshly collected (Table 6A, 6B and 6D) and archived (6C) soil samples, were analyzed by commercial laboratories using Method 8330 and the D TECH™ test kit. The tables provide results for both analyses, and evaluate the agreement between the two.

10.0 REFERENCES

1. D TECH™ TNT Users Guide , SDI/Em Sciences.

2. Haas, R.J., and B.P. Simmons, "Measurement of Trinitrotoluene (TNT) and Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in Soil by Enzyme Immunoassay and High Performance Liquid Chromatography (EPA Method 8330)", California Environmental Protection Agency, Department of Toxic Substances Control, Hazardous Materials Laboratory, March, 1995.

TABLE 1

CROSS REACTANTS - D TECH™ RDX TEST KIT

SAMPLE	MDL[a] (ppb)	IC_{50}[b] (ppb)	% CROSS REACTIVITY[c]
RDX [d]	5	25	100
HMX [d]	150	800	3
TNT (trinitrotoluene)	> 500	> 500	< 1
Tetryl [d]	> 500	> 500	< 1
TNB (trinitrobenzene)	> 500	> 500	< 1
2-amino-4,6-dinitrotoluene	> 500	> 500	< 1
4-amino-2,6-dinitrotoluene	> 500	> 500	< 1
2,4-dinitrotoluene	> 500	> 500	< 1
2,6-dinitrotoluene	> 500	> 500	< 1
1,3-dinitrobenzene	> 500	> 500	< 1
nitrobenzene	> 500	> 500	< 1
2-nitrotoluene	> 500	> 500	< 1
3-nitrotoluene	> 500	> 500	< 1
4-nitrotoluene	> 500	> 500	< 1
nitroglycerine	> 500	> 500	< 1
pentaerythritoltetranitrate	> 500	> 500	< 1

The following compounds were not detected at or above 500 ppm (100x the method MDL for RDX):

Atrazine	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzene
Aroclor 1254	Acenaphthene	Dibenz(ah)anthracene	Chrysene
Acetone	Acenaphthalene	Fluoranthene	Fluorene
Toluene	1,2-Benzanthracene	Benzo(k)fluoranthene	Pyrene
Ethylbenzene	Indeno(123-cd)pyrene	Benzo(ghi)perylene	Xylene
Naphthalene	Methanol	Phenanthrene	

[a] The Method Detection Limit (MDL) is defined as the lowest concentration of compound that yields a positive test result.

[b] The IC_{50} is defined as the concentration of compound required to produce a test response equivalent to 50% of the maximum response.

[c] % Cross Reactivity is determined by dividing the equivalent RDX concentration by the actual compound concentration at IC_{50}.

[d] RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine
HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
Tetryl = methyl-2,4,6-trinitrophenylnitramine

TABLE 2

SOIL MATRIX EFFECTS

Soil ID #	Soil Type	State	D TECH™ Result (ppm)
1	Low OM Clay Loam	DE	< 0.5
2	Sassafras Sandy Loam	DE	< 0.5
3	Cecil Sandy Clay Loam	GA	< 0.5
4	Davidson Clay Loam	GA	< 0.5
5	Shontik-Casa Grande Clay Loam	AZ	< 0.5
6	Trix Sandy Clay Loam	AZ	< 0.5
7	Trix-Casa Grande Clay Loam	AZ	< 0.5
8	Yolo Loam	CA	< 0.5
9	Capay Silty Clay	CA	< 0.5
10	Sycamore Silt Loam	CA	< 0.5
11	Dennis Silt Loam	KA	< 0.5
12	Luray Silty Clay Loam	OH	< 0.5
13	Wooster Silt Loam	OH	< 0.5
14	Vienna Loam	SD	< 0.5
15	Opal Clay	SD	< 0.5
16	Raulb Silt Loam	IN	< 0.5
17	Rockfield Silt Loam	IN	< 0.5
18	Cisne Silt Loam	IL	< 0.5
19	Muscatine Silt Loam	IL	< 0.5
20	Avonburg	IL	< 0.5
21	Matapeake Silt Loam	DE	< 0.5
22	Evesboro Low OM Sand	DE	< 0.5
23	Selbyville High OM Sand	DE	< 0.5
24	Casa Grande Clay Loam	AZ	< 0.5
25	Grundy Silty Clay Loam	KA	< 0.5
26	Drummer Silty Clay	IL	< 0.5
27	Non-Soil Control	-	< 0.5

TABLE 3

FALSE NEGATIVE AND FALSE POSITIVE RATES, SOIL MATRIX[a]

Spike Concentration	False Positive Rate	False Negative Rate
0.25 ppm	0%	-
1.0 ppm	-	0%

[a] Thirty negative soils were spiked with RDX at one-half and two times the MDL (0.25 and 1.0 ppm, respectively). These samples were analyzed with the D TECH™ RDX test kit to determine the error rate of the assay.

TABLE 4

DETERMINATION OF EXTRACTION EFFICIENCY FROM SOIL SAMPLES[a]

Soil ID : Spike (ppm)	Mean RDX Concentration (ppm)	Standard Deviation	Coefficient of Variation (%)	Recovery (%)
101:1	0.53	0.19	35	53
106:1	0.88	0.13	15	88
108:1	0.86	0.23	26	86
109:1	0.66	0.22	34	66
110:1	0.70	0.14	19	70
116:1	0.96	0.12	13	96
117:1	0.92	0.42	46	92
123:1	1.00	0.45	45	100
126:1	1.03	0.25	24	103
128:1	1.02	0.18	18	102
Non-Soil Control:1	1.05	0.13	12	105
Average	0.86	0.23	27	86
101:6	4.92	0.54	11	82
106:6	6.15	0.84	14	103
108:6	5.69	1.09	19	95
109:6	6.11	0.93	15	102
110:6	6.12	0.46	8	102
116:6	6.26	1.21	19	104
117:6	5.71	0.72	13	95
123:6	6.05	0.8	13	101
126:6	6.82	0.33	5	114
128:6	6.02	0.62	10	100
Non-Soil Control:6	6.02	0.83	14	100
Average	5.98	0.75	13	100

TABLE 5

RECOVERY OF RDX SPIKED INTO REAL SOILS.

Soil ID	Spike Concentration (ppm)	Method 8330 (ppm)	D TECH™ (ppm)	AGREEMENT Y, FN, FP
106	0.4	0.32	< 0.5	Y
			< 0.5	Y
			< 0.5	Y
	1.0	0.83	0.5 - 1.5	Y
			0.5 - 1.5	Y
			0.5 - 1.5	Y
	3.0	1.79	> 2.0	FP
			> 2.0	FP
			≥ 2.0	FP
116	0.4	0.29	< 0.5	Y
			< 0.5	Y
			< 0.5	Y
	1.0	0.66	0.5 - 1.5	Y
			0.5 - 1.5	Y
			0.5 - 1.5	Y
	3.0	0.61	> 2.0	FP
			< 2.0	FP
			> 2.0	FP
128	0.4	0.31(0.25)	< 0.5	Y
			< 0.5	Y
			< 0.5	Y
	1.0	0.73(0.73)	< 0.5	FN
			0.5 - 1.5	Y
			0.5 - 1.5	Y
	3.0	0.75(2.27)	≥ 2.0	Y
			< 2.0	Y
			< 2.0	Y

Y = Yes, FN = False Negative, FP = False Positive

TABLE 6A

COMPARISON OF D TECH™ SOIL RESULTS WITH METHOD 8330

Sample ID	Method 8330 (ppm)	D TECH™ (ppm)	AGREEMENT Y, FN, FP
S4	< 0.2	< 0.5	Y
S12	< 0.2	< 0.5	Y
S14	1.72	1.5 - 2.0	Y
S15	< 0.2	< 0.5	Y
S19	2.12	1.5 - 3.0	Y
S20	1.61	1.5 - 3.0	Y
S21	0.32	< 0.5	Y
T1-2	0.21	< 0.5	Y
T2-4	1.41	1.5 - 2.0	FP
T6-1	2.62	> 3.0	FP
T3-5	2.00	0.5 - 1.5	FN
T12-3	< 0.2	< 0.5	Y
T12-6	1.00	0.5 - 1.5	Y
T20-3	< 0.2	< 0.5	Y
T21-10	1.89	1.5 - 2.0	Y
T22-4	< 0.2	< 0.5	Y
T22-5	0.83	0.5 - 1.5	Y
T22-6	0.99	0.5 - 1.5	Y
T28-3	3.73	> 3.0	Y
T28-4	< 0.2	< 0.5	Y
T28-5	< 0.2	< 0.5	Y
T28-6	< 0.2	< 0.5	Y
T28-7	< 0.2	< 0.5	Y
T28-8	< 0.2	< 0.5	Y
T28-9	< 0.2	< 0.5	Y

TABLE 6A (cont.)

Sample ID	Method 8330 (ppm)	D TECH™ (ppm)	AGREEMENT Y, FN, FP
T28-10	0.28	< 0.5	Y
T28-11	1.51	1.5 - 3.0	Y
T28-12	1.3	1.5 - 3.0	FP
T28-13	0.6	0.5 - 1.5	Y
T31-4	1.22	1.5 - 2.0	FP
T12-5	0.26	< 0.5	Y

Y = Yes, FN = False Negative, FP = False Positive

TABLE 6B

COMPARISON OF D TECH™ SOIL RESULTS WITH METHOD 8330

		Replicate 1		Replicate 2	
Sample ID	Method 8330 (ppm)	D TECH™ (ppm)	AGREEMENT Y, FN, FP	D TECH™ (ppm)	AGREEMENT Y, FN, FP
1	4.00	> 3.0	Y	> 3.0	Y
3	19.0	> 6.0	Y	> 6.0	Y
13	1.30	0.5 - 1.5	Y	0.5 - 1.5	Y
15	1.80	1.5 - 3.0	Y	1.5 - 3.0	Y
16	3.40	> 3.0	Y	> 3.0	Y
23	0.48	0.5 - 1.5	Y	0.5 - 1.5	Y
24	0.68	0.5 - 1.5	Y	< 0.5	FN
25	0.68	0.5 - 1.5	Y	0.5 - 1.5	Y
26	0.75	0.5 - 1.5	Y	0.5 - 1.5	Y
31	0.13	0.5 - 1.5	FP	0.5 - 1.5	Y
33	0.74	0.5 - 1.5	Y	0.5 - 1.5	Y
34	0.48	0.5 - 1.5	Y	0.5 - 1.5	Y
35	1.30	1.5 - 3.0	FP	1.5 - 3.0	Y
37	5.50	> 6.0	FP	> 3.0	Y
38	0.55	0.5 - 1.5	Y	0.5 - 1.5	Y
43	1.30	1.5 - 3.0	FP	1.5 - 3.0	FP
44	40.0	> 6.0	Y	> 6.0	Y
47	2.30	> 3.0	FP	> 3.0	FP
48	0.36	0.5 - 1.5	FP	< 0.5	Y
58	0.79	0.5 - 1.5	Y	0.5 - 1.5	Y
59	0.80	1.5 - 3.0	FP	1.5 - 3.0	FP
64	2.20	1.5 - 3.0	Y	1.5 - 3.0	Y
67	10.9	> 6.0	Y	> 6.0	Y
68	3.40	1.5 - 3.0	FN	1.5 - 3.0	Y
75	3.90	> 3.0	Y	> 3.0	Y
84	17.6	> 6.0	Y	> 6.0	Y
85	70.3	> 6.0	Y	> 6.0	Y
87	101	> 6.0	Y	> 6.0	Y
94	1.60	1.5 - 3.0	Y	1.5 - 3.0	Y
96	0.20	< 0.5	Y	< 0.5	Y

TABLE 6B (cont.)

		Replicate 1		Replicate 2	
Sample ID	Method 8330 (ppm)	D TECH™ (ppm)	AGREEMENT Y, FN, FP	D TECH™ (ppm)	AGREEMENT Y, FN, FP
97	5.40	> 3.0	Y	> 3.0	Y
98	< 0.05	< 0.5	Y	< 0.5	Y
99	< 0.05	< 0.5	Y	0.5 - 1.5	FP
105	130	> 60	Y	> 60	Y
111	< 1.0	> 3.0	FP	< 5.0	Y
113	< 1.0	< 5.0	Y	< 0.5	FN
115	3.00	< 5.0	Y	< 0.5	FN
119	36.0	> 30	Y	15 - 30	FN

Y = Yes, FN = False Negative, FP = False Positive

TABLE 6C

COMPARISON OF D TECH™ SOIL RESULTS WITH METHOD 8330

Sample ID	METHOD 8330 (ppm)	D TECH™ (ppm)	AGREEMENT Y, FN, FP
1	17	15 - 30	Y
2	34	15 - 30	FN
3	48	> 30	Y
4	160	60 - 120	FN
5	650	150 - 300	FN
6	41	> 30	Y
7	360	50 - 150	FN
8	840	> 600	Y
9	69	> 60	Y
10	85	30 - 60	FN
19	17	> 6.0	Y
20	19	> 6.0	Y
11	4.3	> 3.0	Y
12	1.9	> 3.0	FP
13	4.9	> 3.0	Y
14	27	1.5 - 3.0	Y
15	1.2	1.5 - 3.0	FP
16	1.0	1.5 - 3.0	FP
17	0.82	0.5 - 1.5	Y
18	0.78	0.5 - 1.5	Y
21	0.67	< 0.5	FN
22	0.94	< 0.5	FN
23	< 0.4	< 0.5	Y
24	< 0.4	< 0.5	Y
25	< 0.4	< 0.5	Y
26	< 0.4	< 0.5	Y

TABLE 6C (cont.)

Sample ID	METHOD 8330 (ppm)	D TECH™ (ppm)	AGREEMENT Y, FN, FP
27	< 0.4	< 0.5	Y
28	< 0.4	< 0.5	Y
29	< 0.4	< 0.5	Y
30	< 0.4	< 0.5	Y

Y = Yes, FN = False Negative, FP = False Positive

TABLE 6D

COMPARISON OF D TECH™ SOIL RESULTS WITH METHOD 8330

Sample	D TECH™ Dilution Factor	D TECH™ Results	8330 Results	AGREEMENT Y, FN, FP
1	1	<0.5	<0.17	Y
2	1	<0.5	<0.17	Y
3	1	<0.5	<0.17	Y
4	1	<0.5	<0.17	Y
5	1	0.5-1.5	<0.17	FP
6	1	<0.5	<0.17	Y
7	1	<0.5	<0.17	Y
8	1	0.5-1.5	<0.17	FP
9	1	<0.5	<0.17	Y
10	1	<0.5	<0.17	Y
11	1	0.5-1.5	<0.17	FP
12	1	0.5-1.5	<0.17	FP
13	1	<0.5	<0.17	Y
14	1	<0.5	<0.17	Y
15	1	<0.5	<0.17	Y
16	1	<0.5	<0.17	Y
17	1	<0.5	<0.17	Y
18	1	<0.5	<0.17	Y
19	1	<0.5	<0.17	Y
20	1	<0.5	<0.17	Y
21	1	<0.5	<0.17	Y
22	1	<0.5	<0.17	Y
23	1	<0.5	<0.17	Y
24	1	0.5-1.5	<0.17	FP

TABLE 6D (cont.)

Sample	D TECH™ Dilution Factor	D TECH™ Results	8330 Results	AGREEMENT Y, FN, FP
25	1	<0.5	<0.17	Y
26	1	<0.5	<0.17	Y
27	1	0.5-1.5	<0.17	FP
28	1	<0.5	<0.17	Y
29	1	<0.5	<0.17	Y
30	1	1.5-3.5	0.17-0.99	FP
31	1	<0.5	<0.17	Y
32	1	0.5-1.5	<0.17	FP
33	1	<0.5	<0.17	Y
34	1	0.5-1.5	0.17-0.99	Y
35	1	0.5-1.5	0.17-0.99	Y
36	1	<0.5	<0.17	Y
37	1	1.5-3.0	1.2	FP
38	1	<0.5	<0.17	Y
39	1	0.5-1.5	<0.17	FP
40	1	<0.5	<0.17	Y
41	1	<0.5	<0.17	Y
42	1	<0.5	3.8	FN
43	1	<0.5	<0.17	Y
44	1	<0.5	<0.17	Y
45	1	<0.5	<0.17	Y
46	1	1.5-3.0	<0.17	FP
47	1	<0.5	<0.17	Y
48	1	0.5-1.5	<0.17	FP
49	1	<0.5	<0.17	Y
50	1	0.5-1.5	<0.17	FP
51	1	<0.5	<0.17	Y

TABLE 6D (cont.)

Sample	D TECH™ Dilution Factor	D TECH™ Results	8330 Results	AGREEMENT Y, FN, FP
52	1	0.5-1.5	0.17-0.99	Y
53	100	50-150	100	Y
54	1	3.0-4.5	<0.17	FP
55	1	3.0-4.5	<0.17	FP
56	1	<0.5	<0.17	Y
57	1	0.5-1.5	<0.17	FP
58	1	<0.5	<0.17	Y
59	1	<0.5	<0.17	Y
60	1	1.5-3.0	1.1	FP
61	1	0.5-1.5	<0.17	FP
62	100	150-300	290	Y
63	10	15-30	46	FN
64	1	1.5-3.0	4.8	FN
65	1	1.5-3.0	0.17-0.99	FP
66	1	3.0-4.5	12	FN
67	100	50-150	150	Y
68	1	0.5-1.5	2.6	FN
69	100	50-150	140	Y
70	1	0.5-1.5	7.8	FN
71	1	1.5-3.0	3.2	FN
72	100	150-300	340	FN
73	10	45-60	55	Y
74	10	>60	67	Y
75	10	30-45	63	FN
76	1	1.5-3.0	2.4	Y
77	1	4.5-6.0	6.4	FP
78	10	>60	73	Y

TABLE 6D (cont.)

Sample	D TECH™ Dilution Factor	D TECH™ Results	8330 Results	AGREEMENT Y, FN, FP
79	10	15-30	14	FP
80	1	0.5-1.5	2.1	FN
81	1	3.0-4.5	2.4	FP
82	1	1.5-3.0	2	Y
83	10	>60	94	Y
84	1	>6	23	Y
85	100	50-150	150	Y
86	10	30-45	34	Y
87	100	50-150	150	Y
88	1	0.5-1.5	1.2	Y
89	1	<0.5	0.17-0.99	Y
90	1	<0.5	<15	Y
91	1	<0.5	<15	Y
92	1	<0.5	<2	Y
93	1	<0.5	<15	Y
94	1	<0.5	<5	Y
95	1	<0.5	<0.17	Y
96	1	<0.5	<15	Y
97	1	<0.5	<5	Y
98	1	<0.5	<0.17	Y
99	1	<0.5	<0.17	Y
100	1	<0.5	<0.17	Y

Y = Yes, FN = False Negative, FP = False Positive

METHOD 5000

SAMPLE PREPARATION FOR VOLATILE ORGANIC COMPOUNDS

1.0 SCOPE AND APPLICATION

1.1 Method 5000 provides general guidance on the selection of sample preparation methods (purge-and-trap, extraction, azeotropic distillation, vacuum distillation, dilution, headspace, etc.) for introducing volatile organic compounds into a detection device (outlined in the determinative methods). The matrices include aqueous, soil/sediment, solid waste, organic solvents, air, and oily waste. Other waste matrices may be adaptable to one or more of the listed preparation methods.

1.2 Method 5000 also provides specific information pertaining to analyte interferences, preparation of calibration and spiking standards, and specific quality control that should be applied to each preparative method.

1.3 The following table is presented as a guide to the sample preparation techniques for volatile organic compounds:

SAMPLE PREPARATION METHODS FOR VOLATILE ORGANICS

Method No.	Matrix	Sample Preparation	Analytes
3585	Oily waste	Solvent dilution	Volatile organics
5021	Solids	Automated headspace	Volatile organics
5030	Aqueous	Purge-and-trap	Volatile organics
5031	Aqueous	Azeotropic distillation	Polar volatile organics
5032	Aqueous & solids	Vacuum distillation	Non polar and polar volatile organics
5035	Solids, organic solvents, oily waste	Closed system purge-and-trap	Volatile organics
5041	Air sampled by VOST	Purge-and-trap from VOST	Volatile POHCs

VOST = Volatile Organic Sampling Train
POHCs = Principal Organic Hazardous Constituents

1.4 Method 3585 provides guidance for dilution and direct injection of oily waste samples (e.g., waste oil or oily waste that passes through the filter during TCLP sample preparation) for volatile organic analysis.

1.5 The following table is presented as a guide to the air sampling methods found in Chapter Ten that can be used in conjunction with the volatile organic determinative methods:

AIR SAMPLING METHODS FOR VOLATILE ORGANIC COMPOUNDS
FROM CHAPTER TEN OF SW-846

Method No.	Air Sampling Method	Sample Preparation	Analytes
0011	Aqueous solution of DNPH	Solvent extraction	Formaldehyde plus aldehydes & ketones
0030	Resin/charcoal	Purge-and-trap by 5041	Volatile organics
0031	Resin/Anasorb 747	Purge-and-trap by 5041	Volatile organics
0040	Tedlar® bag	Direct analysis with sample loop	Volatile organics
0100	DNPH-coated silica gel	Solvent extraction	Formaldehyde plus aldehydes & ketones

DNPH = Dinitrophenylhydrazine

1.6 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

2.0 SUMMARY OF METHOD

2.1 Method 5000 provides general information that is common to each of the methods listed in Sec. 1.0. Specifically, this includes: interference problems that are common to any volatile organic sample preparation method; preparation of calibration standards, internal standards, surrogate spikes, laboratory control samples (LCSs), and matrix spikes; a brief summary of each of the methods; and the specific quality control procedures that should be applied to each of the preparative methods.

2.2 Table 1 provides guidance on which sample preparation methods can be employed in conjunction with each volatile organic determinative method.

3.0 INTERFERENCES

3.1 Samples requiring analysis for volatile organic compounds can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures and to Chapter Four for guidance on the cleaning of glassware.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. To reduce the potential for carryover, the sample purging device must be thoroughly rinsed between samples with an appropriate solvent. Purge and trap devices or headspace devices should be thoroughly baked out between samples. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3.4.1 Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result.

3.4.2 Since methylene chloride will permeate through polytetrafluoroethylene (PTFE) tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing.

3.4.3 Laboratory workers' clothing that has been previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination.

3.4.4 The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and similar precautions must be taken to minimize this problem..

3.5 Interference problems specific to the sample preparation methods are discussed in the individual methods.

4.0 APPARATUS AND MATERIALS

Refer to the specific method of interest for a description of the apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents and other reagents needed.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Stock standards for spiking solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. The stock solutions may be used as calibration standards if dilutions are made in a water-miscible solvent. However, the quality control check sample stock concentrate must be prepared independently from the calibration because it serves as a check on the accuracy of the calibration solution.

5.3.1 Purgeable stock standards - Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. The following sections outline one approach to preparing stock standards.

5.3.1.1 Place about 9.8 mL of methanol in a 10-mL, tared, ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.1.2 Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.1.4 Transfer the stock standard solution into a PTFE-sealed screw-cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light, or as recommended by the supplier of the standard.

5.3.1.5 Refer to the determinative method for holding times of the stock solutions.

5.3.2 Non-purgeable stock standards - Non-purgeable stock solutions may be prepared from pure standard materials or purchased as certified solutions. Refer to the individual determinative method for additional guidance.

5.4 Surrogate standards - A surrogate standard (i.e., a compound that is chemically similar to the analyte group but not expected to occur in an environmental sample) should be added to each sample, blank, laboratory control sample and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated by comparing the measured concentration with the amount added to the sample.

5.4.1 Recommended surrogates for certain analyte groups may be listed in the determinative methods. For methods where no recommended surrogates are listed, the laboratory is free to select compounds that fall within the definition provided above. Even compounds that are on the method analyte list may be used as surrogates as long as historical

data are available to ensure their absence at a given site. Normally, one or more surrogates are added for each analyte group.

5.4.2 Prepare a surrogate spiking concentrate by mixing stock standards prepared above and diluting with a water-miscible solvent. Commercially-prepared spiking solutions are acceptable. The concentration for volatile organic analysis by purge-and-trap should be such that a 10 µL aliquot when added directly to 5 mL of sample provides the concentrations listed in the determinative method. The spiking volumes are normally listed in each preparation method. Where concentrations are not specified, a concentration in the sample of 10 times the estimated quantitation limit is recommended. If the surrogate quantitation limit is unknown, the average estimated quantitation limit of method target analytes may be utilized to estimate a surrogate quantitation limit.

5.5 Matrix spike standards - Prepare a matrix spike concentrate by mixing stock standards as prepared above and diluting with a water-miscible solvent. Commercially-prepared spiking solutions are acceptable. The stock standards are to be independent of the calibration standard.

5.5.1 A few methods provide guidance on concentrations and the selection of compounds for matrix spikes. For example, the recommended purgeable matrix spiking solution for Methods 8021 and 8260 is as follows: Prepare a spiking solution in methanol that contains the following compounds at a concentration of 25 mg/L.

Purgeable organics

1,1-Dichloroethene
Trichloroethene
Chlorobenzene
Toluene
Benzene

The suggested matrix spiking solution in any method may be replaced with a project-specific list of analytes of concern. The spiking concentration employed should correspond to either the applicable regulatory limit or action level for the compound or a concentration in the middle of the calibration range, unless the regulatory limit or action level is lower.

5.5.2 For methods with no guidance, select five or more analytes (select all analytes for methods with five or less) from each analyte group for use in a spiking solution. Where matrix spike concentrations in the sample are not listed it should be at or below the regulatory limit or action level concentration or 1 to 5 times higher than the background concentration, whichever concentration would be larger.

5.6 Laboratory control spike standard - Use the matrix spike standard prepared in Sec. 5.5 as the spike standard for the laboratory control sample (LCS). The LCS should be spiked at the same concentration as the matrix spike.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See Chapters Two and Four for guidance on sample collection, preservation, and handling.

7.0 PROCEDURE

Water, soil/sediment, sludge, and waste samples requiring analysis for volatile organics are extracted and/or introduced into the GC and/or GC/MS system by various methods (see Table 1). This manual contains method choices that are dependent on the matrix, the physical properties of the analytes, the sophistication and cost of equipment available to a given laboratory, and the turn-around time required for sample preparation. The following is a brief summary of each of the sample preparation/introduction techniques:

7.1 Method 3585: This method describes a solvent dilution (hexadecane) technique followed by direct injection into a sensitive GC/MS system for the analysis of volatiles in waste oils. Method 3585 has adequate sensitivity to determine the regulatory concentrations for TCLP oily wastes that pass through the filter. Direct injection is very simple, provides quick turnaround, and requires no special hardware. However, the GC/MS system must be quite sensitive, and direct injection has the potential for instrument contamination and is more subject to matrix difficulties. Method 3585 is best when performing analyses for small groups of samples.

7.2 Method 5021: This method describes an automated headspace analysis for soils and other solid matrices. The solid sample is placed in a tared septum-sealed vial at time of sampling. A matrix modifier is added containing internal and/or surrogate standards. The sample vial is placed into an automated equilibrium headspace sampler which heats the entire sample to 85°C and mixes it by mechanical vibration. A measured volume of headspace is automatically introduced into a GC or GC/MS system for volatile organic analysis. The method is automated and causes no equipment contamination, however, it does require an automated headspace device.

7.3 Method 5030: This method describes the technique of purge-and-trap for the introduction of purgeable organics into a gas chromatograph. This procedure is applicable to aqueous samples and water-miscible extracts prepared by Method 5035. An inert gas is bubbled through the sample, which will efficiently transfer the purgeable organics from the aqueous phase to the vapor phase. The vapor phase is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. Purge-and-trap is easily automated, provides good precision and accuracy, but, is limited to analytes that purge efficiently from water and requires a purge-and-trap device. The system is easily contaminated by samples containing compounds at mg/L concentrations. This procedure may be used for the analysis of gasoline in various aqueous matrices.

7.4 Method 5031: This method describes an azeotropic distillation technique for the analysis of nonpurgeable, water-soluble, volatile organics in aqueous samples. The sample is distilled in an azeotropic distillation apparatus (guidance for an optional micro-distillation apparatus is also included) followed by direct aqueous injection of the distillate into a GC or GC/MS system. The method is not readily automated except for the GC/MS analysis, requires a 1-hour distillation, and is applicable to a limited group of analytes.

7.5 Method 5032: This method describes a closed-system vacuum distillation technique for the analysis of volatile organics including nonpurgeable, water-soluble, volatile organics in aqueous samples, soilds and oily waste. The sample is introduced into a sample flask which is then attached to the vacuum distillation apparatus. The sample chamber pressure is reduced and remains at approximately 10 torr (vapor pressure of water) as water is removed from the sample. The vapor is passed over a condenser coil chilled to a temperature of -10°C or less, which results in the condensation of water vapor. The uncondensed distillate is cryogenically trapped on a section of 1/8 inch stainless steel tubing chilled to the temperature of liquid nitrogen (-196°C). After an

appropriate distillation period, which may vary due to matrix or analyte group, the condensate contained in the cryogenic trap is thermally desorbed and transferred to the gas chromatograph using helium carrier gas. This method very efficiently extracts organics from a variety of matrices. The method requires a vacuum system, cryogenic cooling, and is not readily automated, except for the GC/MS analysis.

7.6 Method 5035: This method describes a closed-system purge-and-trap for the analysis of volatile organics that are purgeable from a solid matrix at 40°C. It is amenable to soil/sediment and any solid waste sample of a consistency similar to soil. It differs from the original soil method in Method 5030 in that a sample (normally 5 g) is placed into the sample vial at time of sampling along with a matrix-modifying solution. The sample remains hermetically sealed from sampling through analysis as the closed-system purge-and-trap device automatically adds standards and then performs the purge-and-trap process. The method provides more accurate data than the original method because the sample container is never opened, minimizing the loss of volatiles through sampling handling. However, it does require a special purge-and-trap device. It also includes a technique for the extraction of oily waste using methanol. This procedure may be used for the analysis of gasoline in various solid matrices.

7.7 Method 5041: This method is applicable to the analysis of sorbent cartridges from a volatile organic sampling train (VOST). The sorbent cartridges are placed in a thermal desorber which, in turn, is attached to a standard purge-and-trap device. Analysis may be by GC or GC/MS.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures. Each laboratory using SW-846 methods should maintain a formal quality assurance program. Each sample preparation batch of 20 or less samples should contain: a method blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate samples; and a laboratory control sample, unless the determinative method provides other guidance.

8.2 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean reference matrix. This will include a combination of the sample preparation method (usually a 5000 series method for volatile organics) and the determinative method (an 8000 series method). The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made.

8.2.1 The reference samples are prepared from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.2.2 The procedure for preparation of the reference sample concentrate is dependent upon the method being evaluated. Guidance for reference sample concentrations for certain methods are listed below. In other cases, the determinative methods contain guidance on preparing the reference sample concentrate and the reference sample. If no guidance is provided, prepare a reference sample concentrate in methanol. Spike the reference sample at the concentration on which the method performance data are based. The spiking volume added to water should not exceed 1 mL/L so that the spiking solvent will not decrease purging

efficiency. If the method lacks performance data, prepare a reference standard concentrate at such a concentration that the spike will provide a concentration in the clean matrix that is 10 - 50 times the MDL for each analyte in that matrix.

The concentration of the target analytes in the reference sample may need to be adjusted to more accurately reflect the concentrations that will be analyzed in the laboratory. If the concentration of an analyte is being evaluated relative to a regulatory limit, see Sec. 8.3.3 for information on selecting an appropriate spiking level.

8.2.3 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds) e.g., organic-free reagent water for the water matrix or sand or soil (free of organic interferences) for the solid matrix. Because of the volatility of these compounds, the spike must be introduced directly into the matrix while the matrix is in a sealed container (e.g., a gas-tight syringe or purge device).

8.2.4 Preparation of reference samples

The following sections provide guidance on the QC reference sample concentrates for many SW-846 determinative methods. The concentration of the target analytes in the QC reference sample for the methods listed below may need to be adjusted to more accurately reflect the concentrations of interest in different samples or projects. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 8.3.3 for information on selecting an appropriate spiking level. In addition, the analyst may vary the concentration of the spiking solution and the volume of solution spiked into the sample. However, because of concerns about the effects of the spiking solution solvent on the sample, the total volume spiked into a sample should generally be held to no more than 200 µL.

8.2.4.1 When analyzing aqueous samples by purge-and-trap Method 5030, prepare reference sample concentrates containing each target analyte at a concentration of 10 mg/L in methanol. For water samples, spike 100 mL of organic-free reagent water with 200 µL which provides a 20 µg/L concentration in the reference sample. Quickly transfer the spiked water to four, 5-mL gas-tight syringes. The samples are ready for analysis using Method 5030 and the appropriate determinative method.

8.2.4.2 When analyzing soil or other solid samples by purge-and-trap by Method 5035, add 10 µL of reference sample concentrate directly to the purge device as specified in Sec. 7.0. For oily waste analysis by Method 3585 or the high concentration technique in Method 5035, add 10 µL of reference sample concentrate (dissolved in methanol) directly to the oily waste just prior to the addition of the extraction solvent. The concentration in the oily waste should be 10 - 50 times greater than the determinative method MDL for each analyte. Prepare four replicates.

8.2.4.3 When analyzing matrices using equilibrium headspace by Method 5021 or vacuum distillation by Method 5032, prepare the reference sample concentrate as per Sec. 8.2.4.1. Reference sample concentrates and spiking solutions used in azeotropic distillation Method 5031 should be prepared in water, not alcohol or acetone. Add sufficient reference sample concentrate to the volume of organic-free reagent water specified in these methods to provide a concentration in the water that is 10 - 50 times greater than the determinative method MDL for each analyte. Prepare four replicates.

8.2.4.4 For Methods 8031, 8032, 8315 and 8316, analyze four portions of the water sample volume specified in each method, spiked at a concentration that is 10 - 50 times greater than the determinative method MDL for each analyte.

8.2.5 Analyze replicate aliquots (at least four) of the well-mixed reference samples by the same procedures used to analyze actual samples (Sec. 7.0 of each of the methods). This will include a combination of the sample preparation method (usually a 5000 series method for volatile organics) and the determinative method (an 8000 series method). Follow the guidance on data calculation and interpretation presented in Method 8000, Sec. 8.0.

8.3 Sample Quality Control for Preparation and Analysis

8.3.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair per analytical batch. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. See Sec. 5.5 for additional guidance on matrix spike preparation. Sec. 8.3.3 provides guidance on establishing the concentration of the matrix spike compounds in the sample chosen for spiking. The choice of analytes to be spiked should reflect the analytes of interest for the specific project. Thus, if only a subset of the list of target analytes provided in a determinative method are of interest (e.g., Method 8260 is used for the analysis of only aromatics), then these would be the analytes of interest for the project. In the absence of project-specific analytes of interest, it is suggested that the laboratory periodically change the analytes that are spiked with the goal of obtaining matrix spike data for most, if not all, of the analytes in a given determinative method.

8.3.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

For the laboratory control sample, use a clean matrix for spiking purposes (one that does not have any target or interference compounds) e.g., organic-free reagent water for the water matrix or sand or soil (free of organic interferences) for the solid matrix. Because of the volatility of these compounds, the spike must be introduced directly into the matrix while the matrix is in a sealed container (e.g., a gas-tight syringe or purge device).

8.3.3 The concentration of the matrix spike sample and/or the LCS should be determined as described in the following sections.

8.3.3.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory limit or action level, the spike should be at or below the regulatory limit or action level or 1 - 5 times the background concentration (if historical data are available), whichever concentration is higher.

8.3.3.2 If historical data are not available, it is suggested that an uncontaminated sample of the same matrix from the site be submitted for matrix spiking

purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculation of recoveries.

8.3.3.3 If the concentration of a specific analyte in a sample is not being checked against a limit specific to that analyte, then the spike should be at the same concentration as the reference sample (Sec. 8.2.4) or 20 times the estimated quantitation limit (EQL) in the matrix of interest. It is again suggested that a background sample of the same matrix from the site be submitted as a sample for matrix spiking purposes.

8.3.4 Analyze these QC samples (the LCS and the matrix spikes or the optional matrix duplicates) following the procedure (Sec. 7.0) of the selected determinative method. Calculate and evaluate the QC data as outlined in Sec. 8.0 of Method 8000.

8.3.5 Blanks - Use of method blanks and other blanks are necessary to track contamination of samples during the sampling and analysis processes. Refer to Chapter One for specific quality control procedures.

8.3.6 Surrogates - A surrogate standard is a compound that is chemically similar to the analyte group but not expected to occur in an environmental sample. Surrogate standards should be added to all samples when specified in the appropriate determinative method. See Sec. 5.4 for additional guidance on surrogates.

8.4 The laboratory must have procedures in place for documenting and charting the effect of the matrix on method performance. Refer to Chapter One and Method 8000 for specific guidance on developing method performance data.

9.0 METHOD PERFORMANCE

9.1 The recovery of surrogate standards is used to monitor unusual matrix effects, sample processing problems, etc, in each sample. The recovery of matrix spiking compounds, when compared to laboratory control sample (LCS) recoveries, indicates the presence or absence of unusual matrix effects.

9.2 The performance of each 5000 series method will be dictated by the overall performance of the sample preparation in combination with the analytical determinative method.

10.0 REFERENCES

None required.

TABLE 1

COMBINATIONS OF VOLATILE ORGANIC SAMPLE PREPARATION
AND DETERMINATIVE METHODS FOR SW-846

Determinative Method		Preparation Methods			
No.	Method Title	Aqueous Samples	Soil/Solid Samples	Waste Samples	Air Samples
8011	EDB & DBCP by GC/ECD	8011	None listed	None listed	None listed
8015	Nonhalogenated VOCs by GC/FID	5030, 5031, 5032	5021, 5031 5032, 5035	5032, 5035	None listed
8021	Aromatic and Halogenated VOCs by GC/ELCD & PID	5030, 5032	5021, 5032, 5035	5032, 5035	None listed
8031	Acrylonitrile by GC/NPD	8031, 5030, 5032	5032, 5035	5032, 5035	None listed
8032	Acrylamide by GC/ECD	8032	None listed	None listed	None listed
8033	Acetonitrile by GC/NPD	5031	None listed	None listed	None listed
8260	Volatile Organic Compounds by GC/MS	5030, 5031, 5032	5021, 5031 5032, 5035	5032, 5035	0030, 0031/ 5041, 0040
8315	Carbonyl Compounds by HPLC	8315	8315	8315	0011, 0100/ 8315
8316	Acrylamide and Acrylonitrile by HPLC	8316	None listed	None listed	None listed

DBCP = 1,2-Dibromo-3-chloropropane
EDB = Ethylene dibromide (1,2-dibromoethane)
VOCs = Volatile Organic Compounds
GC = Gas Chromatography
ECD = Electron Capture Detector
ELCD = Electrolytic Conductivity Detector
FID = Flame Ionization Detector
HPLC = High Performance Liquid Chromatography
MS = Mass Spectrometry
PID = Photoionization Detector

VOLATILE ORGANIC COMPOUNDS IN SOILS AND OTHER SOLID MATRICES USING EQUILIBRIUM HEADSPACE ANALYSIS

1.0 SCOPE AND APPLICATION

1.1 Method 5021 is a general purpose method for the preparation of volatile organic compounds (VOCs) in soils/sediments and solid wastes for determination by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS). The method is applicable to a wide range of organic compounds that have sufficiently high volatility to be effectively removed from soil samples using an equilibrium headspace procedure. The following compounds have been determined in soils using Method 5021.

Compound	CAS No.[a]
Benzene	71-43-2
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Methylene chloride	75-09-2
Naphthalene	91-20-3
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,4-Trichlorobenzene	120-82-1

(continued)

Compound	CAS No.[a]
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3
Gasoline Range Organics	

[a] Chemical Abstract Service Registry Number

1.2 Method detection limits, using Method 8260, are compound-, matrix-, and instrument-dependent, and vary from approximately 0.1 to 3.4 µg/kg. The applicable concentration range of this method is approximately 10 µg/kg to 200 µg/kg. Analytes that are inefficiently extracted from the soil will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient concentrations.

1.3 The following compounds may also be analyzed by this procedure or may be used as surrogates.

Compound	CAS No.[a]
Bromobenzene	108-86-1
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
cis-1,2-Dichloroethene	156-59-4
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
n-Propylbenzene	103-65-1
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8

[a] Chemical Abstract Service Registry Number

1.4 Alternatively, the method may be utilized as an automated sample introduction device as a means for screening samples for volatile organics. A suggested configuration is to employ it with Method 8021 but use very minimal calibration and quality control, i.e., a reagent blank and a single calibration standard, to obtain semiquantitative data.

1.5 Method 5021 may be applicable to other compounds that have sufficient volatility to be removed from the soil matrix using the conditions described in this method. It may also be applicable to both listed and non-listed target analytes in other matrices. For solid samples that contain more than 1% organic matter or for compounds with high octanol/water partitioning coefficients, the equilibrium headspace technique may yield slightly lower results then either dynamic purging or methanol extraction followed by dynamic purging.

1.6 This method is restricted to use by, or under the supervision of, analysts experienced in volatile organic analysis in general and specifically the use of equilibrium headspace devices interfaced to the determinative method selected by the analyst.

2.0 SUMMARY OF METHOD

2.1 At least 2 g of a soil sample are placed into a crimp-seal or screw-top glass headspace vial at time of sampling.

2.2 A matrix modifying solution is added to each soil sample to act as a chemical preservative. In addition, each sample is fortified with internal standards and surrogate compounds. These additions may be done either in the field or in the laboratory upon receipt of samples.

2.3 Additional sample volume is collected in a VOA vial for dry weight determination and for high concentration determination if the sample concentration requires it.

2.4 In the laboratory, the vials are rotated to allow for diffusion of the internal standards and surrogates throughout the matrix. The vials are placed in the autosampler carousel of the headspace analyzer and maintained at room temperature. Approximately 1 hour prior to analysis, the individual vials are moved to a heated zone and allowed to equilibrate. The sample is then mixed by mechanical vibration while the elevated temperature is maintained.

2.5 The autosampler then pressurizes the vial with helium which forces a portion of the headspace gas mixture through a heated transfer line onto the GC column.

2.6 Determinative analysis is performed using the appropriate GC or GC/MS method.

3.0 INTERFERENCES

3.1 Volatile organic analyses are subject to major interference problems because of the prevalence of volatile organics in a laboratory. See Method 5000, Sec. 3.0, for common problems and precautions to be followed.

3.2 The sample matrix itself can cause severe interferences by one of several processes or a combination of these processes. These include, but are not necessarily limited to, the absorption potential of the soil, the biological activity of the soil, and the actual composition of the soil. Soils high in oily material and organic sludge wastes inhibit the partitioning of the volatile target analytes

into the headspace, therefore, recoveries will be low. This so- called "matrix effect" can be difficult, if not impossible, to overcome. It is recommended that surrogates or additional deuterated compounds (for GC/MS methods) be added to a matrix and analyzed to determine the percent recovery of these compounds. The calculated percent recovery can give some indication of the degree of the matrix effect, but not necessarily correct for it. Alternatively, the use of the high concentration procedure in this method should minimize the problem with oily waste and other organic sludge wastes.

4.0 EQUIPMENT AND SUPPLIES

4.1 Sample Containers - Clear glass, 22-mL soil vials, compatible with the analytical system. The vial must be capable of being hermetically sealed in the field (either crimp-cap or screw-cap) and be equipped with a polytetrafluoroethylene (PTFE)-lined septum which demonstrates minimum bleed at elevated temperatures while maintaining the seal. Ideally, the vials and septa should have a uniform tare weight. Prior to use, wash the vials and septa with detergent solution, then rinse with tap water followed by distilled water. Dry the vials and septa in an oven at 105°C for 1 hour, then remove and allow to cool. Store in an area free of organic solvents. Vials of other sizes may be employed, provided that they can be hermetically sealed and equipped with a suitable septum.

4.2 Headspace System - This method was developed using a totally automated equilibrium headspace analyzer, the Tekmar Model 7000 Equilibrium Headspace Autosampler and a Tekmar 7050 Carousel (Tekmar Co., 7143 East Kemper Road, Cincinnati, OH 45249). Similar systems are available from several commercial sources. The system used must meet the following specifications.

4.2.1 The system must be capable of holding samples at elevated temperatures and establishing a reproducible equilibrium between a wide variety of sample types and the headspace.

4.2.2 The system must be capable of accurately transferring a representative portion of the headspace into a gas chromatograph fitted with a capillary column. This must be accomplished without adversely affecting the chromatography or the detector.

4.2.3 The operating conditions listed in Sec. 7.0 are those selected for the equipment used in developing this method. Other equipment and conditions may be employed, provided that the laboratory demonstrates performance for the analytes of interest using the determinative method appropriate for the intended application.

4.3 Field Sampling Equipment

4.3.1 A soil sampler which delivers at least 2 g of soil is necessary, e.g., Purge-and-Trap Soil Sampler Model 3780SPT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.3.2 An automatic syringe or bottle-top dispenser calibrated to deliver 10.0 mL of matrix modifier solution, e.g., Automatic Vaccinator Model C1377SN (NASCO, 901 Jamesville Ave., P.O. Box 901, Fort Atkinson, WI 53538), or equivalent.

4.3.3 An automatic syringe calibrated to deliver internal standards and surrogate analytes.

4.3.4 Crimping tool for sample vials. If using screw-top vials, this is not needed.

4.4 Miscellaneous Equipment

4.4.1 VOA vials - 40 or 60 mL VOA vials with PTFE-faced septa and crimp-seal caps or screw-top caps. These vials will be used for sample screening, high concentration analysis (if needed) and dry weight determination.

5.0 REAGENTS

5.1 Organic-Free Reagent Water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH_3OH - Pesticide quality or equivalent. Store away from other solvents. Purchase in small quantities (½ Liter or 1 Liter size) to minimize contamination.

5.3 See the determinative method and Method 5000 for guidance on the preparation of stock standards and a secondary standard for internal standards, calibration standards, and surrogates.

5.3.1 Calibration spiking solutions - Prepare five spiking solutions in methanol that contain all the target analytes and the surrogate standards. The concentrations of the calibration solutions should be such that the addition of 1.0 µL of each to the 22 mL vials will bracket the analytical range of the detector, e.g., for Method 8260 the suggested concentration range for target analytes and surrogates is 5, 10, 20, 40 and 50 mg/L. The suggested concentration of internal standards is 20 mg/L (internal standards may be omitted for the GC methods if desired). The internal standard may be added separately using 1.0 µL or premixed with the calibration standards maintaining a 20 mg/L concentration in each calibration standard. These concentrations may vary depending on the relative sensitivity of the GC/MS system or any other determinative method that is utilized.

5.3.2 Internal and surrogate standards - Follow the recommendations of the determinative methods for the selection of internal and surrogate standards. A concentration of 20 mg/L in methanol for both internal and surrogate standards will be needed for spiking each sample. If determination is by GC, external standard calibration may be preferred and the internal standard is omitted. The concentration may vary depending on the relative sensitivity of the GC/MS system or any other determinative method that is utilized.

5.4 Blank Preparation - Transfer 10.0 mL (Sec. 5.6) of matrix modifying solution to a sample vial. Add the prescribed amounts of the internal standards and surrogate compounds, and seal the vial. Place it in the autosampler and analyze in the same manner as an unknown sample. Analyzing the blank in this way will indicate possible problems with the autosampler as well as the headspace device.

5.5 Preparation of Calibration Standards - Prepare calibration standards in the same manner as the blanks (Sec. 5.4) using the standards prepared in Sec. 5.3.1.

5.6 Matrix Modifying Solution - Using a pH meter, add concentrated phosphoric acid (H_3PO_4) dropwise to 500 mL of organic-free reagent water until the pH is 2. Add 180 g of NaCl. Mix well until all components are dissolved. Analyze a 10.0 mL portion from each batch per Sec. 5.4 to verify that the solution is free of contaminants. Store in a sealed bottle in an area free of organic chemicals at 4°C.

WARNING: The matrix modifying solution may not be appropriate for soil samples having organic carbon content. See Sec. 6.2.4.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Three alternative procedures are presented for the collection of low concentration samples in special headspace sample vials. One procedure includes the addition of a matrix modifying solution and standards in the field while the other two procedures do not. The choice between these alternatives should be based on knowledge of the field conditions, the organic carbon content of the soil, the specific volatile analytes of interest, and the intended use of the analytical results. Whichever alternative is used, collect 3 or 4 vials of sample from each sampling point to allow for sample reanalyses if necessary. In addition, separate portions of sample are taken for dry weight determination and for high concentration analysis (if necessary).

The addition of the matrix modifying solution and the internal and surrogate standards at the time of sampling (Sec. 6.2) is the preferred option unless high concentrations of volatile organics are expected. The matrix modifying solution eliminates biodegradation of the analytes, minimizes losses of analytes by volatility since the vial is not opened in the laboratory, and minimizes dehydrohalogenation reactions through pH adjustment.

The downside is increased opportunity for contamination of the matrix modifier and standards in a field sampling situation. Also, skilled personnel are required to precisely and accurately add the matrix modifying solution, and especially the internal and surrogate standards.

These problems are minimized when these solutions are not added in the field (Sec. 6.1), however, there is the likelihood of significant losses of volatile analytes when the vial is reopened in the laboratory.

If high concentrations of volatile organics are expected (greater than 200 µg/kg), collection of the sample in the 22-mL vial without the addition of the matrix modifying solution allows direct addition of methanol to the vial, as described in the high concentration method in Sec. 7.5.

6.1 Sample collection without the addition of matrix modifying solution and standards

6.1.1 Use standard 22-mL crimp-cap or screw-top glass headspace vials with PTFE-faced septa (other vials may be used, as described in Sec. 4.1).

6.1.2 Using the purge-and-trap soil sampler (Sec. 4.3.1), add 2-3 cm (approximately 2 g) of the soil sample to a tared 22-mL headspace vial and seal immediately with the PTFE side of the septum facing toward the sample. The samples should be introduced into the vials gently to reduce agitation which might drive off volatile compounds.

6.2 Sample collection with the addition of matrix modifying solution and standards

6.2.1 Use standard 22-mL crimp-cap or screw-top glass headspace vials with PTFE-faced septa (other vials may be used, as described in Sec. 4.1).

6.2.2 Add 10.0 mL of matrix modifying solution to the vial prior to adding the sample.

6.2.3 Using the purge-and-trap soil sampler (Sec. 4.3.1), add 2-3 cm (approximately 2 g) of the soil sample to a tared 22-mL headspace vial. The samples should be introduced

into the vials gently to reduce agitation which might drive off volatile compounds. Seal the vial immediately with the PTFE side of the septum facing toward the sample.

6.2.4 Using an appropriate size syringe (e.g., 10 µL), carefully puncture the septum and add the amount of internal and surrogate standards called for in the determinative method.

WARNING: Preliminary indications are that soil samples containing over 1% organic carbon may yield low recoveries when the matrix modifying solution is used. The matrix modifying solution may not be appropriate for these samples.

6.3 The third alternative is to add the soil sample to a vial containing 10.0 mL of organic-free reagent water. This organic-free reagent water may be added to the vial either in the field or in the laboratory prior to shipping the vials to the field.

6.3.1 Use standard 22-mL crimp-cap or screw-top glass headspace vials with PTFE-faced septa (other vials may be used, as described in Sec. 4.1).

6.3.2 Using the purge-and-trap soil sampler (Sec. 4.3.1), add 2-3 cm (approximately 2 g) of the soil sample to a tared 22-mL headspace vial containing 10.0 mL of reagent water. The samples should be introduced into the vials gently to reduce agitation which might drive off volatile compounds. Seal immediately with the PTFE side of the septum facing toward the sample.

6.4 Field blanks should be prepared, regardless of which alternative is employed for the soil samples. If the matrix modifying solution is not added in the field, then the field blank should be prepared by adding 10.0 mL of organic-free reagent water to a clean vial and immediately sealing the vial. If the matrix modifying solution and standards are added in the field, then prepare a field blank by adding 10.0 mL of matrix modifying solution plus internal and surrogate standards to a clean vial.

6.5 Fill a 40- or 60-mL VOA vial with soil from each sampling point to use for dry weight determination, sample screening, and for high concentration analysis (if necessary). Sample screening is optional since there is no danger of contaminating the headspace device because of carryover from a high concentration sample.

6.6 Sample Storage

6.6.1 Store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.6.2 All samples should be analyzed within 14 days of collection. Samples not analyzed within this period must be identified to the data user and the results are considered minimum values.

7.0 PROCEDURE

7.1 Sample screening

This method (using the low concentration approach), used in conjunction with either Methods 8015 (GC/FID) or 8021 (GC/PID/ELCD), may be used as a sample screening method prior to any

of the sample introduction - GC/MS configurations to assist the analyst in determining the approximate concentration of volatile organics present in a sample. This is especially critical prior to the use of volatile organic analysis by purge-and-trap to prevent the contamination of the system by high concentration samples. It can also be helpful prior to the use of this headspace method, to determine whether to proceed with the low concentration method or the high concentration method. High concentrations of volatiles will not contaminate the headspace device. However, it may create contamination problems in the GC or GC/MS system. Whenever this method is utilized for sample screening, very minimal calibration and QC are suggested. In most cases, a reagent blank and a single point calibration are sufficient.

7.2 Determination of sample % dry weight

In certain cases, sample results are desired based on dry-weight basis. When such data are desired, a portion of sample for this determination should be weighed out from the 40 or 60 mL VOA vial (Sec. 6.5.3).

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\%\ \text{dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 The Low Concentration Method utilizing an equilibrium headspace technique is found in Sec. 7.4 and sample preparation for the High Concentration Method is found in Sec. 7.5. The high concentration method is recommended for samples that obviously contain oily material or organic sludge waste (see Sec. 3.3). See Method 5000, Sec. 7.0, for guidance on the selection of a GC or GC/MS determinative method. For the analysis of gasoline, use Method 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons. If GC/MS analysis is preferred for BTEX in gasoline, follow Method 8260.

7.4 Low concentration method for soil/sediment and solid waste amenable to the equilibrium headspace method. (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.4.1 Calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods because of possible interference problems with internal standards. If interferences are not a problem, based on historical data, internal standard calibration is acceptable. The GC/MS methods normally utilize internal standard calibration. The GC/MS methods require instrument tuning prior to proceeding with calibration.

7.4.1.1 GC/MS tuning

If a GC/MS determinative method is employed, prepare a 22-mL vial containing reagent water and the amount of BFB specified in the determinative method.

7.4.1.2 Initial calibration

Prepare five 22-mL vials, as described in Sec. 5.5, and a reagent blank (Sec. 5.4), and proceed according to Sec. 7.4.2 and the determinative method selected. The mixing step is eliminated since no soil is present in the vial.

7.4.1.3 Calibration verification

Prepare a 22-mL vial, as described in Sec. 5.5, by spiking with the mid-concentration calibration standard. Proceed according to Sec. 7.4.2.4 (beginning by placing the vial into the autosampler) and the determinative method. If a GC/MS determinative method is employed, prepare a second 22-mL vial containing reagent water and the amount of BFB specified in the determinative method.

7.4.2 Headspace operating conditions

The conditions described throughout Sec. 7.4 were experimentally optimized using the equipment described in Sec. 4.2.1 and employing Method 8260 as the determinative method. If other headspace systems and determinative methods are utilized, it is recommended that the manufacturer's headspace operating conditions be followed, provided that they are appropriate for the determinative method to be employed.

7.4.2.1 This method is designed for a 2-g sample size. The sample is prepared in the field by adding 2 g of the soil sample to the 22 mL crimp-seal or screw-top glass headspace vial as described in Sec. 6.0.

7.4.2.2 Prior to analysis, weigh the sealed vial and its contents to 0.01 g. If the matrix modifying solution was added at the time of sampling (Sec. 6.2), the tare weight does not include the 10 mL of matrix modifying solution. Therefore, weigh the field blank and determine the weight of the matrix modifying solution in the field blank and use that weight as the weight of the matrix modifying solution in the samples. (Although this approach may introduce some error into the sample results, that error should be much less than the changes that will occur in an unpreserved sample shipped to the laboratory without the modifier).

7.4.2.3 If the matrix modifying solution was not added at the time of sampling (Sec. 6.1), unseal the vial, rapidly add 10.0 mL of matrix modifying solution and the amount of internal standard and surrogate standards called for in the determinative method, and immediately reseal the vial. As noted in the introductory text in Sec. 6.0, volatilization losses will occur as a result of opening the vial and displacing 10 mL of air.

NOTE: Only open and prepare one vial at a time to minimize loss of volatile organics.

7.4.2.4 Mix the samples (on a rotator or shaker) for at least 2 min. Place the vials in the autosampler carrousel at room temperature. The individual vials are heated to 85°C and allowed to equilibrate for 50 min. Each sample is mixed by mechanical

vibration for at least 10 min during this equilibrium period. Each vial is pressurized with helium carrier gas to a minimum pressure of 10 psi.

7.4.2.5 A representative and reproducible sample of the pressurized headspace is transferred to the GC column through a heated transfer line according to the manufacturer's instructions.

7.4.2.6 Proceed with the analysis as per the determinative method of choice.

7.5 High concentration method

7.5.1 If the sample was collected as described in Sec. 6.1 without the addition of matrix modifying solution or organic-free reagent water to the vial, then weigh the sample to the nearest 0.01 g, add 10.0 mL of methanol to the sample in the tared 22-mL vial, and immediately reseal the vial. Open only one vial at a time to minimize the loss of volatile organics.

7.5.2 If the procedures in either Sec. 6.2 or 6.3 were employed for sample collection and either the matrix modifying solution or organic-free reagent water were added to the vial, then the sample for high concentration analysis should be taken from the separate 40- or 60-mL VOA vial filled in the field. Transfer approximately 2 g of sample from the 40- or 60-mL VOA vial into a tared 22-mL sample vial. Immediately add 10.0 mL of methanol to the 22-mL vial and seal both the 22-mL and the VOA vials. Open only one vial at a time to minimize the loss of volatile organics.

7.5.3 Mix by shaking for 10 min at room temperature. Decant 2 mL of the methanol to a screw-top vial with PTFE-faced septa and seal. Withdraw 10 µL, or appropriate volume of extract from Table 2, and inject into a 22 mL vial containing 10.0 mL of matrix modifying solution and internal standards (if required) and surrogates. Analyze by the headspace procedure by placing the vial into the autosampler and proceeding with Sec. 7.4.2.4.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each

set of samples to be analyzed. This includes the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS) and the addition of surrogates to each sample and QC sample.

8.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

Single laboratory accuracy and precision data were obtained for the method analytes in two soil matrices: sand and a surface garden soil. These data are found in tables in Method 8260.

10.0 REFERENCES

1. Flores, P., Bellar, T., "Determination of Volatile Organic Compounds in Soils using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry," U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Cincinnati, OH, December, 1992.

2. Ioffe, B.V., Vitenberg, A.G., "Headspace Analysis and Related Methods in Gas Chromatography," John Wiley and Sons, 1984.

TABLE 1

DETERMINATIVE METHODS COMPATIBLE WITH METHOD 5021

Method Number	Method Title
8015	Nonhalogenated Volatile Organics Using GC/FID
8021	Aromatic and Halogenated Volatiles by GC with Detectors in Series
8260	Volatile Organics by GC/MS

TABLE 2

QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-CONCENTRATION SOILS/SEDIMENTS

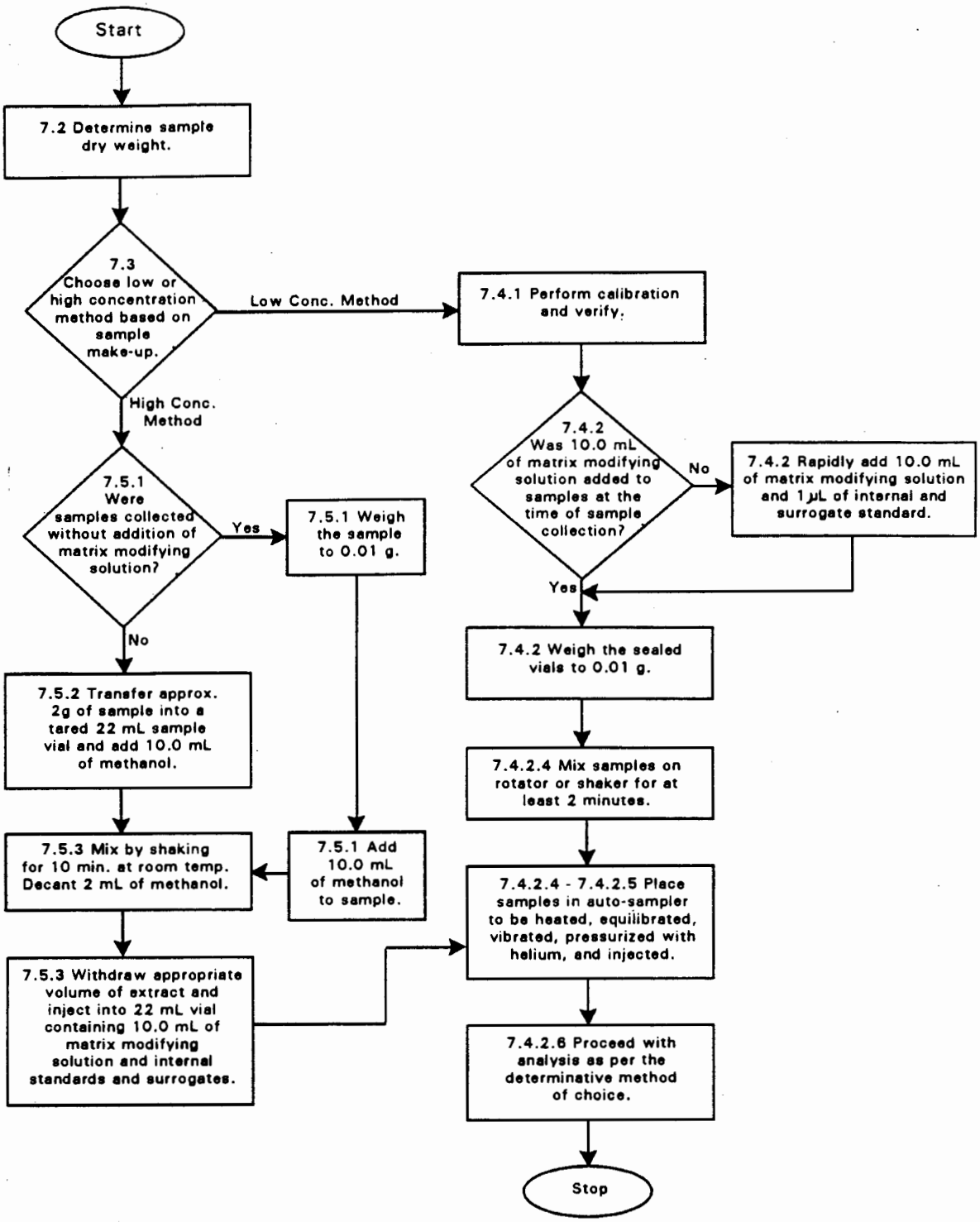
Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 µg/kg	100 µL
1,000-20,000 µg/kg	50 µL
5,000-100,000 µg/kg	10 µL
25,000-500,000 µg/kg	100 µL of 1/50 dilution [b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

VOLATILE ORGANIC COMPOUNDS IN SOILS AND OTHER SOLID MATRICES
USING EQUILIBRIUM HEADSPACE ANALYSIS



METHOD 5030B

PURGE-AND-TRAP FOR AQUEOUS SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of high concentration soil and waste sample extracts prepared in Method 5035. The gas chromatographic determinative steps are found in Methods 8015 and 8021. The method is also applicable to GC/MS Method 8260.

1.2 Method 5030 can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3 Method 5030, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5030 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Methods 8021 GC/PID) in series with Method 8015.

1.4 Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Aqueous Samples: An inert gas is bubbled through a portion of the aqueous sample at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

2.2 High Concentration Extracts from Method 5035: An aliquot of the extract prepared in Method 5035 is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS following the normal aqueous method.

3.0 INTERFERENCES

3.1 Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

3.4 The laboratory where volatiles analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage areas should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL. These syringes should be equipped with a 20-gauge (0.006 in ID) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Two 5-mL glass hypodermic syringes with Luer-Lok tip (other sizes are acceptable depending on sample volume used).

4.4 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.5 Vials - 2-mL, for GC autosampler.

4.6 Purge-and-trap device

The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.6.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be used, provided equivalent or improved performance is demonstrated.

4.6.2 The trap used to develop this method was 25 cm long with an inside diameter of 0.105 in. Starting from the inlet, the trap contains the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.6.3 The desorber must be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

4.6.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

4.6.5 Trap Packing Materials

4.6.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.6.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.6.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.6.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.6.5.5 Alternate Trap Materials

A number of hydrophobic carbon molecular sieve and graphitized carbon black materials have been developed. Various combinations of these materials have been shown to provide retention properties similar to the Tenax\Silica gel\Carbon trap. Alternate trap construction with such materials is allowed, provided that the adsorption and desorption characteristics obtained achieve equivalent or better method sensitivity and precision in comparison to the performance documented in the Determinative Method.

4.6.5.5.1 The following alternatives have been shown to be viable for most analytes of concern:

7.6-cm Carbopack™ B/1.3-cm Carboseive™ S-III
VOCARB 3000 - 10.0-cm Carbopack™ B/6.0-cm Carboxin ™ 1000/1.0-cm Carboxin™ 1001
VOCARB 4000 - 8.5-cm Carbopack™ C/10.0-cm Carbopack ™ B/6.0-cm Carboxin™ 1000/1.0-cm Carboxin™ 1001

These combinations require rapid heating to desorption temperatures of 245°C to 270°C (follow manufacturer's instructions). At these increased temperatures, catalytic and thermal decomposition of analytes has been reported. The VOCARB 4000 combination has also been demonstrated to catalytically break down 2-chloroethyl vinyl ether, and to partially decompose 2,2-dichloropropane. Bromoform and bromomethane have shown some thermal decomposition.

4.6.5.5.2 The amount of thermal decomposition products formed must be routinely tracked by daily monitoring of the formation of chloromethane and bromomethane. A daily check standard containing surrogates, internal standards, and 20 µg/L bromoform must be analyzed prior to the analysis of the daily check standard. If levels of chloromethane or bromomethane exceed 0.5 µg/L, then the trap may be too contaminated with salts or tightly bound contamination for analysis to continue. The trap must be replaced and the system recalibrated.

NOTE: Even newly constructed traps may have become contaminated prior to their first use from airborne vapors. These highly adsorptive materials must be kept tightly sealed in an area of minimum organic vapor contamination.

4.7 Heater or heated oil bath - capable of maintaining the purging chamber to within 1°C, over a temperature range from ambient to 100°C.

4.8 Capillary GC Columns - Any GC column that meets the performance specifications of the determinative method may be used. See the specific determinative method for recommended columns, conditions and retention times.

4.8.1 The wide-bore columns have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface , an all-glass jet

separator, or a cryogenic (Sec. 4.8.2) device are acceptable interfaces. The type of interface and its adjustments can have a significant impact on the method detection limits. Other interfaces can be used if the performance specifications described in this method can be achieved.

4.8.2 A system using a narrow-bore column will require lower gas flows of approximately 2 - 4 mL/minute. Because of these low desorption flows, early eluting analytes need to be refocussed to elute in a narrow band. This refocussing may be carried out by using a cryogenic interface. This type of interface usually uses liquid nitrogen to condense the desorbed sample components in a narrow band on an uncoated fused silica precolumn. When all components have been desorbed form the trap, the interface is rapidly heated under a stream of carrier gas to transfer the analytes to the analytical column. The end of the analytical column should be placed within a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by ice caused by desorbing water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution. Low surrogate compound recoveries can be a sign that this is occurring.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 See the determinative method and Method 5000 for guidance on internal and surrogate standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Sec. 4.1. Samples should be stored in capped bottles, with minimum headspace, at 4°C or less in an area free of solvent fumes. The size of any bubble caused by degassing upon cooling the sample should not exceed 5 - 6 mm. When a bubble is present, also observe the cap and septum to ensure that a proper seal was made at time of sampling. Is there any evidence of leakage? If the sample was improperly sealed, the sample should be discarded.

6.2 All samples should be analyzed within 14 days of collection. Samples not analyzed within this period must be noted and data are considered minimum values.

7.0 PROCEDURE

7.1 The purge-and-trap technique for aqueous samples is found in Sec. 7.2 and guidance for analysis of solvent extracts from the High Concentration Method in Method 5035 is found in Sec. 7.3. The gas chromatographic determinative steps are found in Methods 8015 and 8021. The method is also applicable to GC/MS Method 8260. For the analysis of gasoline, use Method 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons.

7.2 This section provides guidance on the analysis of aqueous samples and samples that are water miscible, by purge-and-trap analysis.

7.2.1 Initial calibration

Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the specific determinative methods and Method 5000 give details on preparation of standards. The GC/MS methods require instrument tuning prior to proceeding with calibration.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.6. Condition the Tenax trap overnight at 180°C (condition other traps at the manufacturers recommended temperature) in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.1.2 Connect the purge-and-trap device to a gas chromatograph or gas chromatograph/mass spectrometer system.

7.2.1.3 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of organic-free reagent water to the purging device. The organic-free reagent water is added to the purging device using a 5-mL glass syringe (a 10-mL or 25-mL syringe may be used if preferred) fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10-µL or 25-µL micro-syringe equipped with a long needle (Sec. 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards. Add the aliquot of calibration solution directly to the organic-free reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe, be sure that the end of the syringe needle is well beneath the surface of the organic-free reagent water. Similarly, add 10.0 µL of the internal standard solution. Close the 2-way syringe valve at the sample inlet. (The calibration standard, internal standard and surrogate standard may be added directly to the organic free reagent water in the syringe prior to transferring the water to the purging device, see Sec. 7.2.4.7).

7.2.1.4 Follow the purge-and-trap analysis as outlined in Sec. 7.2.4.

7.2.1.5 Calculate response factors (RF) or calibration factors (CF) for each analyte of interest using the procedure described in Method 8000.

7.2.1.6 The average CF (external standards) or RF (internal standards) must be calculated for each compound. For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.6.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.1.6.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.6.3 1,1,2,2-Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.7 The analytes in Method 8021 normally are not as strongly affected by small changes in purge flow or system contamination. When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross contamination and memory effects from a high concentration sample or even the standard are a common problem. Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification: Refer to Method 8000 for details on calibration verification.

7.2.2.1 To prepare a calibration standard, inject an appropriate volume of a primary dilution standard to an aliquot of organic free reagent water in a volumetric flask, a gas tight syringe, or to a purge device, and inject an appropriate amount of internal standard to the organic free reagent water. Be sure the same amount of internal standard is added to each standard and sample. The volume of organic free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL). The surrogate and internal standard solutions must be added with a syringe needle long enough to ensure addition below the surface of the water. Assemble the purge-and-trap device as outlined in 4.6. Follow the guidance for the purge-and-trap procedure in Sec. 7.2.4. Ongoing GC or GC/MS calibration criteria must be met as specified in Method 8000 before analyzing samples.

7.2.3 Sample screening

7.2.3.1 Screening of the sample prior to purge-and-trap analysis may provide guidance on whether sample dilution is necessary and may prevent contamination of the purge-and-trap system.

7.2.3.2 SW-846 contains two screening techniques that may be utilized: the automated headspace sampler (Method 5021) connected to a gas chromatograph equipped with a photoionization detector in series with an electrolytic conductivity detector; and extraction of the samples with hexadecane (Method 3820) and analysis of the extract on a gas chromatograph equipped with a flame ionization detector and/or electron capture detector. In addition, other appropriate screening techniques may be employed at the discretion of the analyst.

7.2.4 Sample introduction and purging

7.2.4.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.2.4.2 Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in Sec. 7.0 of the specific determinative method to be employed. Whole oven cooling may be needed for certain GC columns and/or certain GC/MS systems to achieve adequate resolution of the gases. Normally a 30 meter wide-bore column will require cooling the GC oven to 25°C or below for resolution of the gases.

7.2.4.3 GC or GC/MS calibration verification criteria must be met (Method 8000) before analyzing samples.

7.2.4.4 Adjust the purge gas flow rate (nitrogen or helium) to 25-40 mL/min (also see Table 1 for guidance on specific analyte groups), on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.2.4.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. Alternatively, carefully transfer the remaining sample into a 20-mL VOA vial. Seal the vial with zero headspace. The second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 10- or 25-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hrs. Care must be taken to prevent air from leaking into the syringe.

7.2.4.6 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.2.4.6.1 Dilutions may be made in volumetric flasks (10-mL to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.2.4.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.2.4.6.3 Inject the proper aliquot of samples from the syringe prepared in Sec. 7.2.4.5 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions.

7.2.4.6.4 Fill a 5-mL syringe with the diluted sample as in Sec. 7.2.4.5.

7.2.4.7 Add 10.0 µL of surrogate spiking solution (found in each determinative method, Sec. 5.0) and, if applicable, 10.0 µL of internal standard spiking solution through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Matrix spiking solutions, if indicated, should be added (10.0 µL) to the sample at this time.

7.2.4.8 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.2.4.9 Close both valves and purge the sample for the time and at the temperature specified in Table 1. For GC/MS analysis using Method 8260, purge time is 11 minutes at ambient temperature.

7.2.5 Sample desorption

The procedures employed for sample desorption depend on the type of GC interface used. Procedures for non-cryogenic and cryogenic interfaces are described below. Analysts should also consult the instructions from the manufacturer of the purge-and-trap system and the supplier of the trap packing material.

7.2.5.1 Non-cryogenic interface - After the recommended 11-minute purge (see Table 1 for guidance on purge times for specific analyte groups), place the purge-and-trap system in the desorb mode and preheat the trap to 180°C (or other temperature recommended for the specific trap packing material) without a flow of carrier gas passing through the trap.

NOTE: Some purge-and-trap systems are capable of performing a moisture removal step (e.g., dry purge) which can eliminate excess moisture from the trap and gas lines by purging the trap just prior to the desorption step. However, the utility of a moisture removal step depends on the nature of the trap packing material. In general, when using a carbon-based, hydrophobic trap packing, this step may prevent moisture from entering the GC system and affecting chromatography, but may require that the trap be cooled to keep the temperature at or below 25°C. However, for packings that are less hydrophobic or hydrophilic (such as silica gel), a moisture removal step may actually create more significant problems, including loss of sensitivity, poor chromatography, and premature failure of the trap packing material, through the release of increasing amounts of water into the GC system during the course of an analytical shift. The problem may be evident as erratic responses for the early-eluting internal standards and surrogates over the course of the day. Optimum results may be achieved through the proper choices of: the moisture control device, the trap packing material, trap temperature during moisture removal, and carrier gas flow. The use of trap back pressure control may also be necessary. Consult instructions from both the manufacturer of the purge-and-trap system and the supplier of the trap packing material before employing a moisture removal step.

Start the flow of the carrier gas, begin the GC temperature program, and start GC data acquisition. The carrier gas flow rate will depend on the trap employed. A flow rate of 15 mL/min is used for the standard silica gel trap (Sec. 4.6.2), while 10 mL/min may

be adequate for other traps. Continue the carrier gas flow for about 4 min, or as recommended by the manufacturer. Desorption times as low as 1.5 min may be adequate for analytes in Method 8015.

7.2.5.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure the cryogenic interface is -150°C or lower, and rapidly heat the trap to 180°C (temperature may vary depending on the trap material) while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Method 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C; simultaneously begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.6 Trap Reconditioning

7.2.6.1 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C for Methods 8021 and 8260, and 210°C for Method 8015. Trap temperatures up to 220°C may be employed. However, the higher temperatures will shorten the useful life of the trap. (Trap temperatures may vary depending on the trap material). After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.2.6.2 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of organic free reagent water (or methanol followed by organic free reagent water) to avoid carryover of volatile organics into subsequent analyses.

7.2.7 Interpretation and calculation of data

7.2.7.1 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated response from a compound, this analysis must be followed by the analysis of organic free reagent water. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can meet the organic-free reagent water criteria specified in Chapter One.

7.2.7.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Method 8000 and the specific determinative method for details on calculating analyte response.

7.2.8 Analysis of water-miscible liquids

7.2.8.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with organic-free reagent water.

7.2.8.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample into a 100-mL volumetric flask and diluting to volume with organic-free reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.2.8.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with organic-free reagent water by adding at least 20.0 µL, but not more than 100.0 µL of liquid sample. The sample is ready for addition of surrogate and, if applicable, internal and matrix spiking standards.

7.3 This section provides guidance on the analysis of solvent extracts from High Concentration Samples prepared by Method 5035.

7.3.1 The GC or GC/MS system should be set up as in Sec. 7.0 of the specific determinative method. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.3.2 Table 2 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100.0 µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.3.3 Remove the plunger from a 5.0-mL Luer-lok type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10.0 µL of internal standard solution. Also add the volume of solvent extract determined in Sec. 7.3.2 and a volume of the same solvent used in Method 5035 to total 100.0 µL (excluding methanol in standards).

7.3.4 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.3.5 Proceed with the analysis as outlined in the specific determinative method. Analyze all reagent blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100.0 µL of methanol to simulate the sample conditions.

7.4 Sample analysis

The samples prepared by this method may be analyzed by Methods 8015, 8021, and 8260. Refer to these methods for appropriate analysis conditions. For the analysis of gasoline, use Method 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be

processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Each analysis batch of 20 or less samples must contain: a reagent blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis; and a laboratory control sample, unless the determinative method provides other guidance.

8.4 Surrogate standards should be added to all samples when specified in the appropriate determinative method

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

TABLE 1

PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method	
	8015	8021/8260
Purge gas	N_2 or He	N_2 or He
Purge gas flow rate (mL/min)	20	40
Purge time (min)	15.0 ±0.1	11.0 ±0.1
Purge temperature (°C)	85 ±2	Ambient
Desorb temperature (°C)	180	180
Backflush inert gas flow (mL/min)	20-60	20-60[1]
Desorb time (min)	1.5	4

[1] The desorption flow rate for Method 8021 with a wide bore capillary column will optimize at approximately 10 to 15 mL/minute.

TABLE 2

QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 µg/kg	100 µL
1,000-20,000 µg/kg	50 µL
5,000-100,000 µg/kg	10 µL
25,000-500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

FIGURE 1
EXAMPLE OF PURGING DEVICE

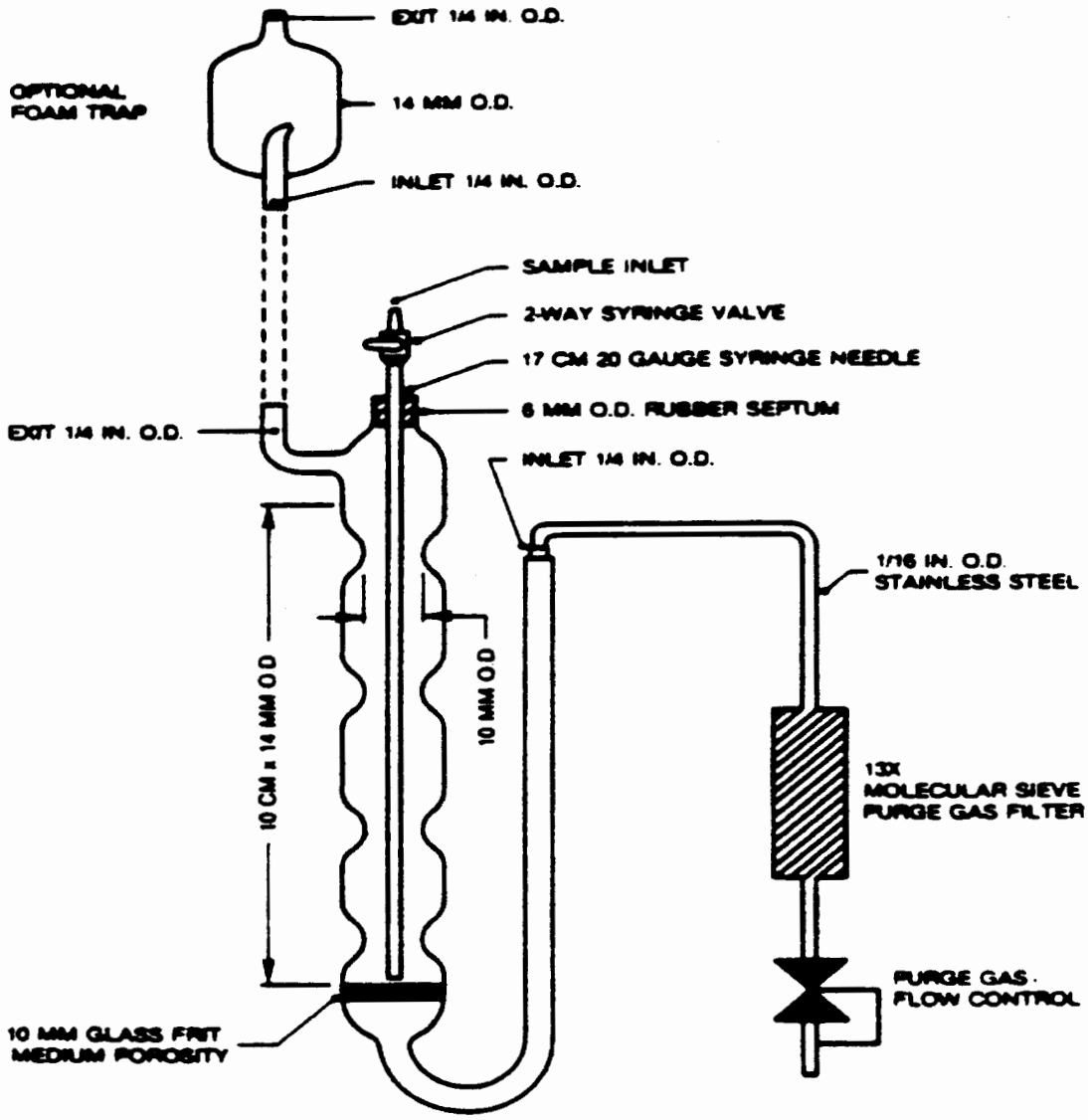


FIGURE 2
EXAMPLE OF TRAP PACKINGS AND CONSTRUCTION
TO INCLUDE DESORB CAPABILITY

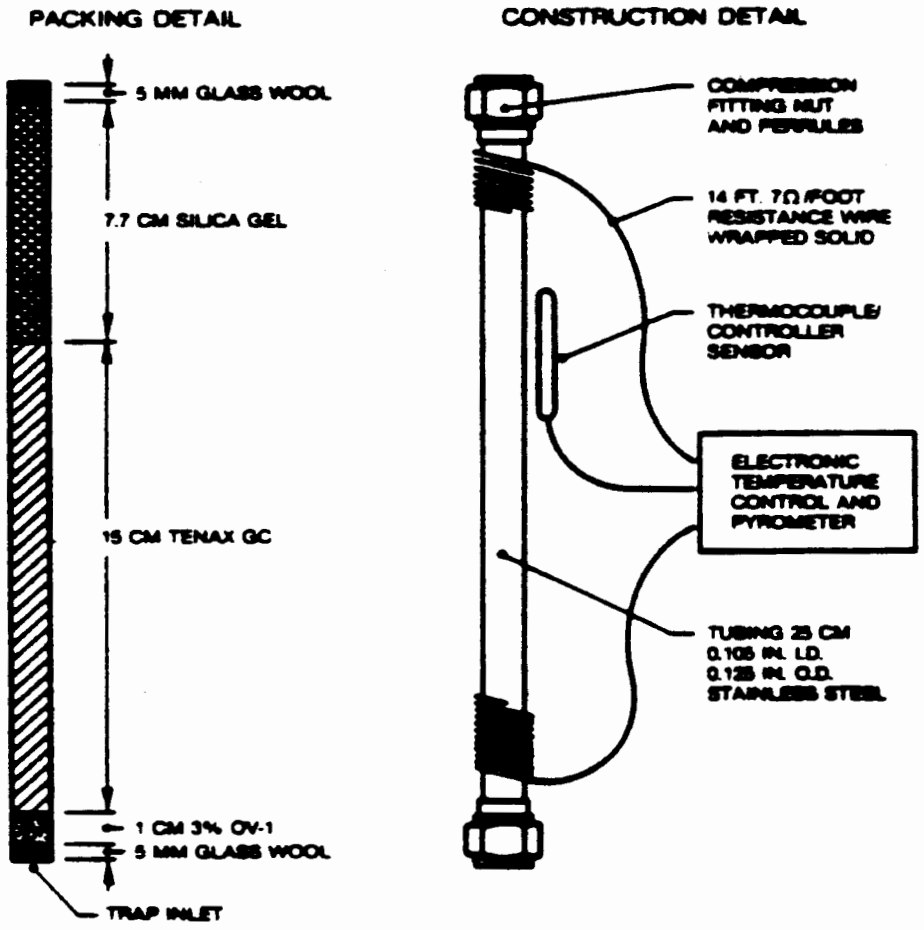


FIGURE 3
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
PURGE MODE

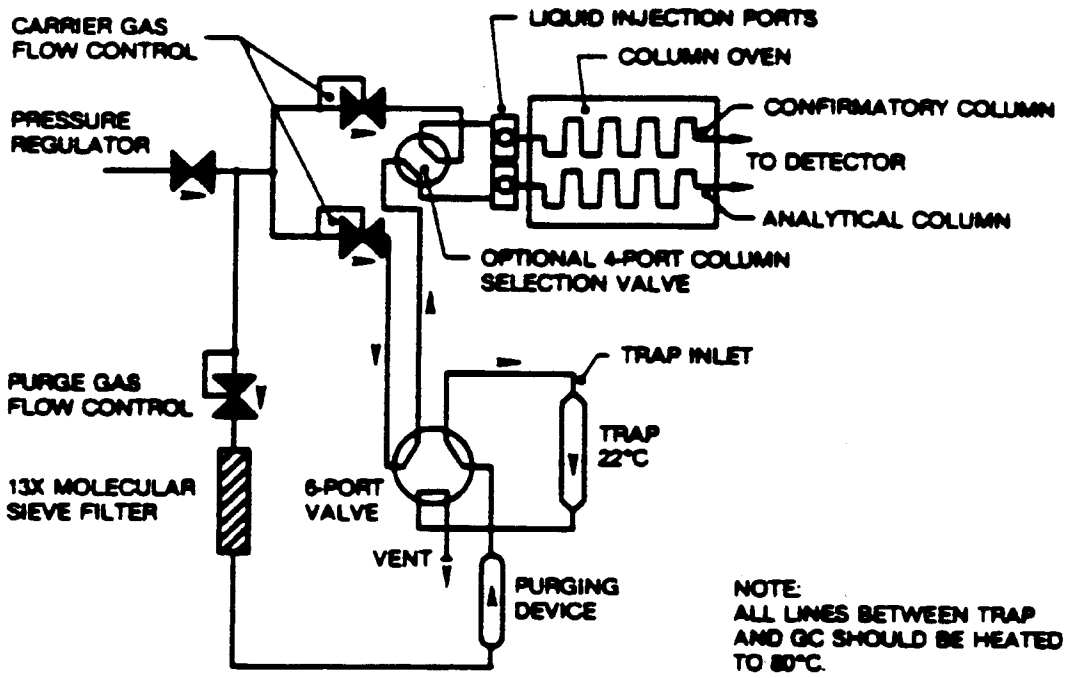
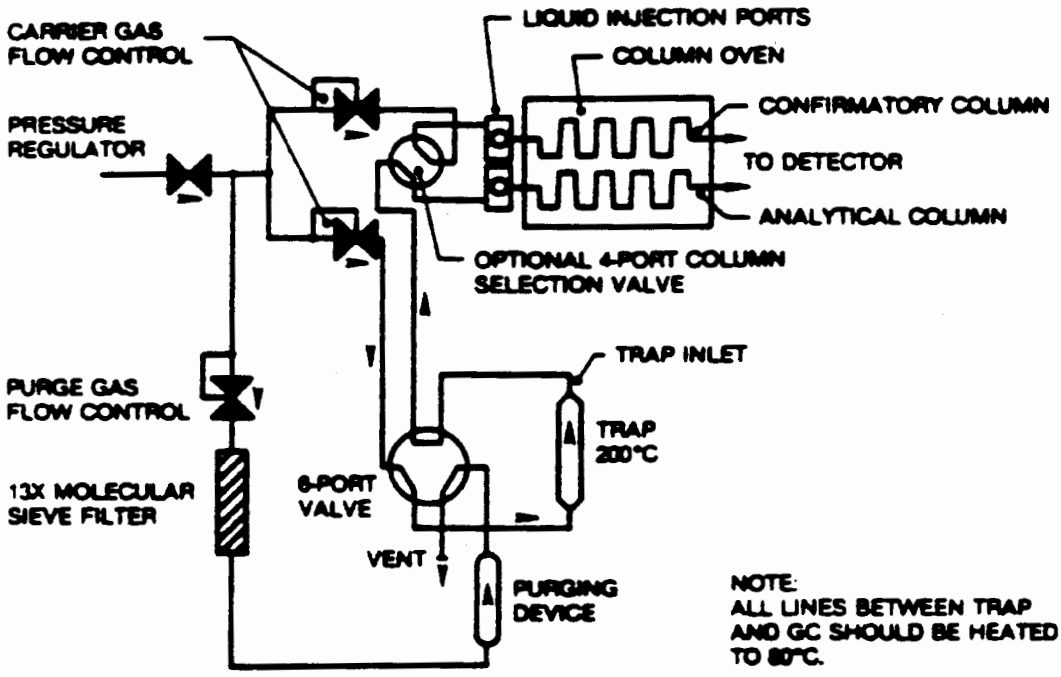
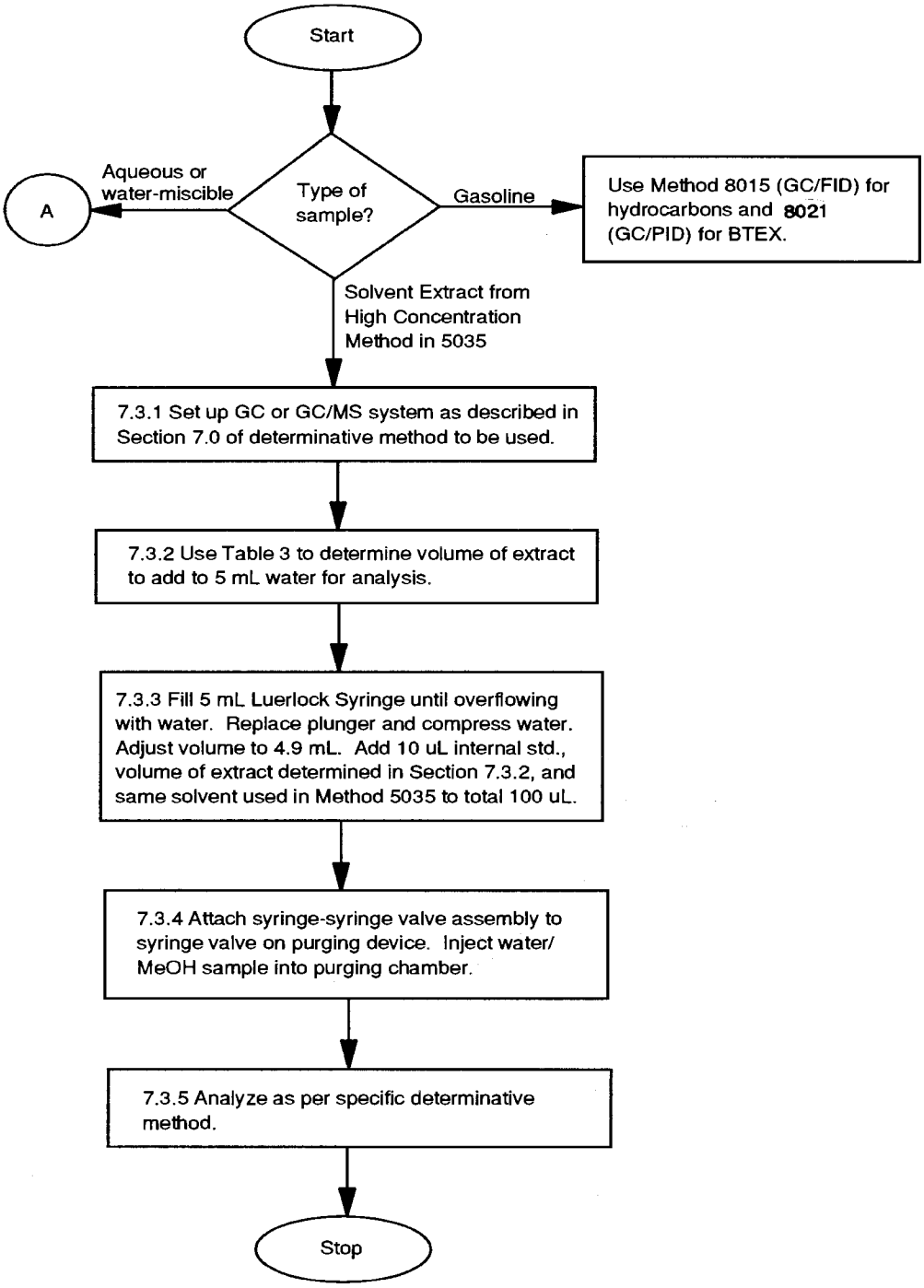
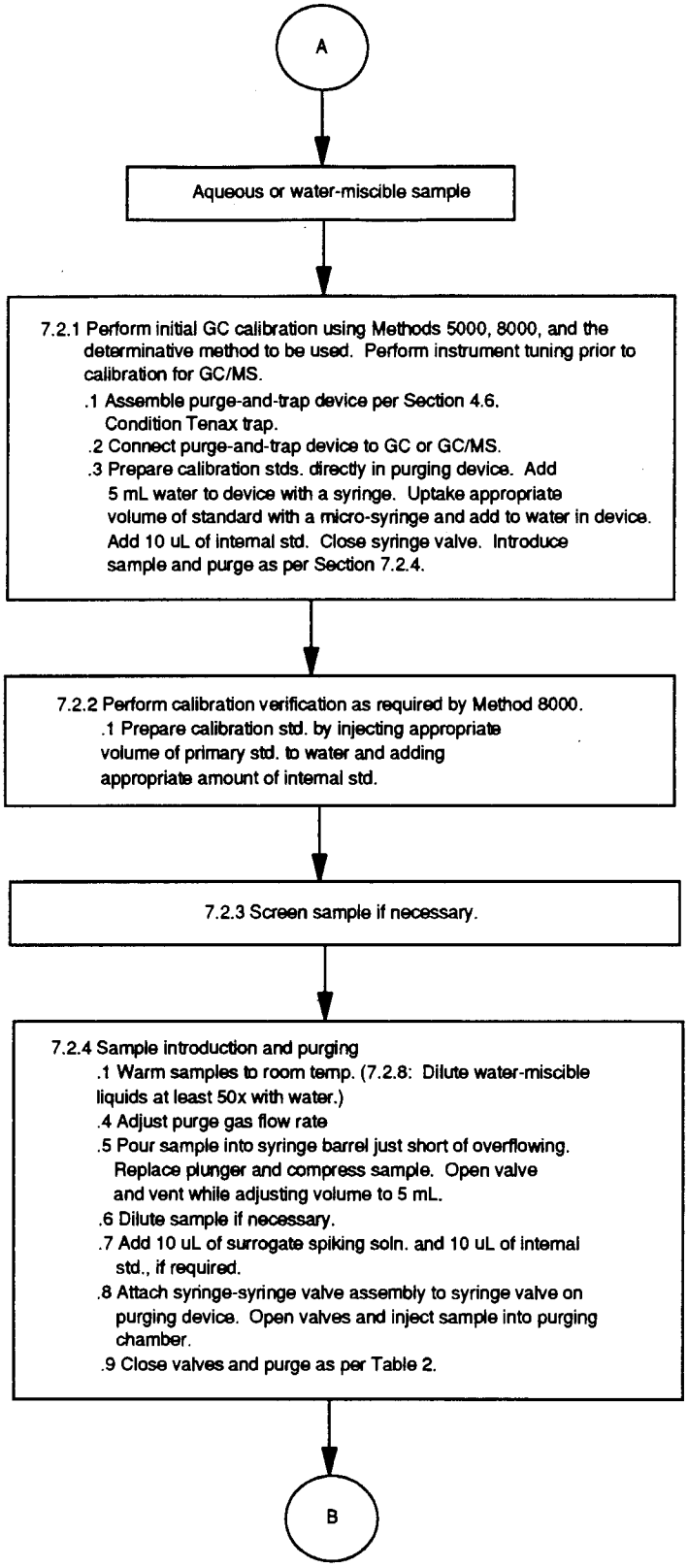
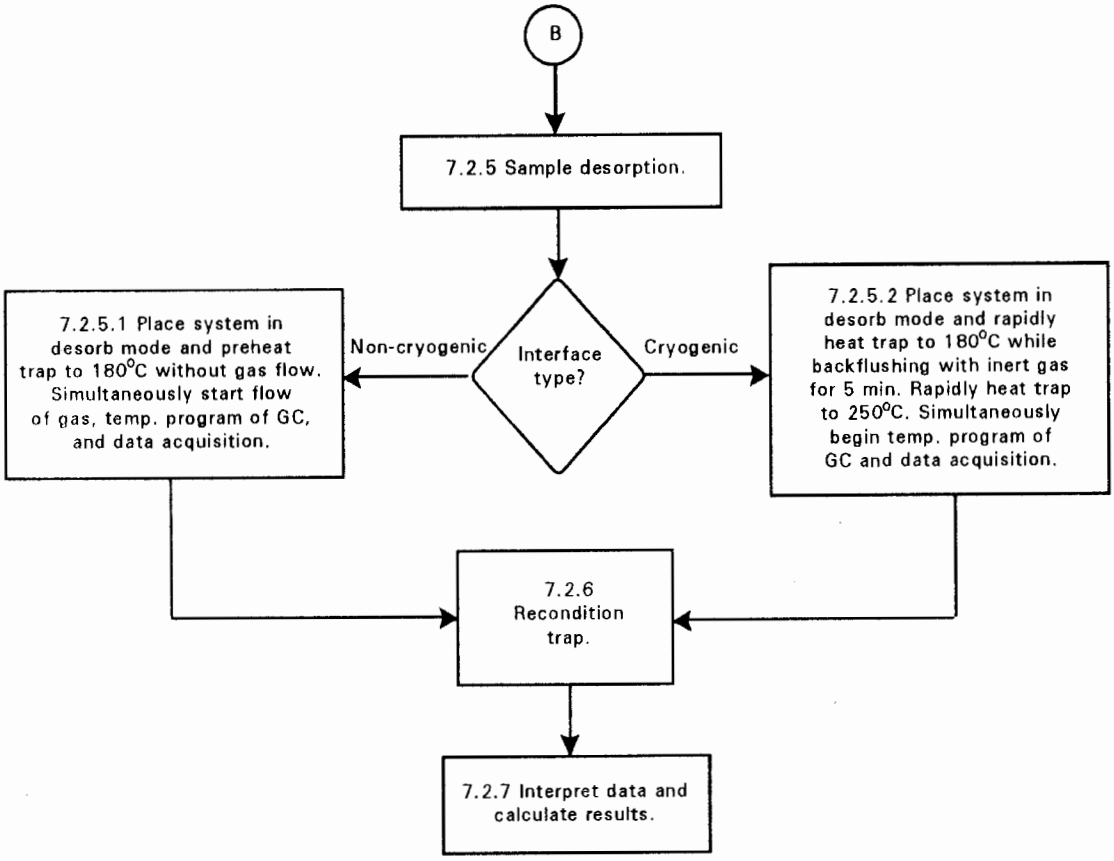


FIGURE 4
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
DESORB MODE




Start
Type of sample?
Aqueous or water-miscible
A
Gasoline
Use Method 8015 (GC/FID) for hydrocarbons and 8021 (GC/PID) for BTEX.
Solvent Extract from High Concentration Method in 5035
7.3.1 Set up GC or GC/MS system as described in Section 7.0 of determinative method to be used.
7.3.2 Use Table 3 to determine volume of extract to add to 5 mL water for analysis.
7.3.3 Fill 5 mL Luerlock Syringe until overflowing with water. Replace plunger and compress water. Adjust volume to 4.9 mL. Add 10 uL internal std., volume of extract determined in Section 7.3.2, and same solvent used in Method 5035 to total 100 uL.
7.3.4 Attach syringe-syringe valve assembly to syringe valve on purging device. Inject water/ MeOH sample into purging chamber.
7.3.5 Analyze as per specific determinative method.
Stop


A
Aqueous or water-miscible sample
7.2.1 Perform initial GC calibration using Methods 5000, 8000, and the determinative method to be used. Perform instrument tuning prior to calibration for GC/MS.
.1 Assemble purge-and-trap device per Section 4.6. Condition Tenax trap.
.2 Connect purge-and-trap device to GC or GC/MS.
.3 Prepare calibration stds. directly in purging device. Add 5 mL water to device with a syringe. Uptake appropriate volume of standard with a micro-syringe and add to water in device. Add 10 uL of internal std. Close syringe valve. Introduce sample and purge as per Section 7.2.4.
7.2.2 Perform calibration verification as required by Method 8000.
.1 Prepare calibration std. by injecting appropriate volume of primary std. to water and adding appropriate amount of internal std.
7.2.3 Screen sample if necessary.
7.2.4 Sample introduction and purging
.1 Warm samples to room temp. (7.2.8: Dilute water-miscible liquids at least 50x with water.)
.4 Adjust purge gas flow rate
.5 Pour sample into syringe barrel just short of overflowing. Replace plunger and compress sample. Open valve and vent while adjusting volume to 5 mL.
.6 Dilute sample if necessary.
.7 Add 10 uL of surrogate spiking soln. and 10 uL of internal std., if required.
.8 Attach syringe-syringe valve assembly to syringe valve on purging device. Open valves and inject sample into purging chamber.
.9 Close valves and purge as per Table 2.
B


B
7.2.5 Sample desorption.
Interface type?
Non-cryogenic
Cryogenic
7.2.5.1 Place system in desorb mode and preheat trap to 180°C without gas flow. Simultaneously start flow of gas, temp. program of GC, and data acquisition.
7.2.5.2 Place system in desorb mode and rapidly heat trap to 180°C while backflushing with inert gas for 5 min. Rapidly heat trap to 250°C. Simultaneously begin temp. program of GC and data acquisition.
7.2.6 Recondition trap.
7.2.7 Interpret data and calculate results.

METHOD 5031

VOLATILE, NONPURGEABLE, WATER-SOLUBLE COMPOUNDS BY AZEOTROPIC DISTILLATION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for separation of nonpurgeable, water-soluble, and volatile organic compounds in aqueous samples or leachates from solid matrices using azeotropic distillation. The appropriate gas chromatographic/mass spectrometric (GC/MS) determinative steps are found in Method 8260. The appropriate gas chromatographic/flame ionization (GC/FID) determinative steps are found in Method 8015. This separation method should be used as an alternative to Method 5030 for compounds that are difficult to purge and trap. Method 5031 is useful in the determination of the following compounds:

Compound Name	CAS No.[a]
Acetone	67-64-1
Acetonitrile	75-05-8
Acrylonitrile	107-13-1
Allyl alcohol	107-18-6
1-Butanol	104-51-8
t-Butyl alcohol	75-65-0
Crotonaldehyde	123-73-9
1,4-Dioxane	123-91-1
Ethanol	64-17-5
Ethyl Acetate	141-78-6
Ethylene oxide	75-21-8
Isobutyl alcohol	78-83-1
Methanol	67-56-1
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
N-Nitroso-di-n-butylamine	924-16-3
Paraldehyde	123-63-7
2-Pentanone	107-87-9
2-Picoline	109-06-8
1-Propanol	71-23-8
2-Propanol	67-63-0
Propionitrile	107-12-0
Pyridine	110-86-1
o-Toluidine	95-53-4

[a] Chemical Abstract Service Registry Number

1.2 Additional compounds may be separated successfully using this method. However, use of this method to detect and measure additional analytes may be done only after the laboratory obtains acceptable accuracy and precision data for each additional analyte. In general, compounds that form a water azeotrope that is greater than 50% analyte, with this azeotrope boiling at less than

100°C, can be successfully distilled. The initial study (Reference 5) to determine the ability of this method to separate compounds found that the following compounds perform poorly in this method:

Compound	CAS No.	Compound	CAS No.
Acrolein	107-02-8	Methacrylonitrile	126-98-7
Aniline	62-53-3	Phenol	108-95-2
Dimethylformamide	68-12-2	Propargyl alcohol	107-19-7
2-Ethoxyethanol	110-80-5		

1.3 The method detection limits (MDLs) and analyte concentration ranges are listed in the appropriate determinative methods. The MDL for a sample may differ from those listed, depending on the nature of interferences in the sample matrix.

1.4 This method is restricted to use by or under the supervision of analysts experienced in procedures involving quantitative separation techniques. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 An azeotrope is a liquid mixture of two or more substances which behaves like a single substance, in that it boils at a constant temperature and the vapors released have a constant composition. Azeotropic distillation is a technique which uses the ability of selected organic compounds to form binary azeotropes with water to facilitate the separation of the compounds from a complex matrix.

2.2 Macrodistillation technique: One liter of the sample is buffered to pH 7, spiked with the surrogate spiking solution, and brought to boiling in a 2 L distillation flask. The polar, volatile organic compounds (VOCs) distill into the distillate chamber for 1 hour, and are retained there (Figure 1). The condensate overflows back into the pot and contacts the rising steam. The VOCs are stripped by the steam and are recycled back into the distillate chamber. Analytes are detected and quantitated by either direct aqueous injection GC/MS or GC/FID.

2.3 Microdistillation technique: An aliquot (normally 5 g or 40 mL) of sample is azeotropically distilled, and the first 100 µL to 300 µL of distillate are collected. The water soluble volatile organic compounds are concentrated into the distillate using a microdistillation system. Most semi- and non-volatile interferences remain in the boiling flask. Use of an internal standard is recommended to improve method precision. Concentration factors are typically one and two orders of magnitude for soil and water matrices, respectively. The distillation takes five to six minutes. Analytes are detected and quantitated by either direct aqueous injection GC/MS or GC/FID.

3.0 INTERFERENCES

3.1 Method interference may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with methanol, followed by a distilled water rinse and drying in a

105°C oven between analyses. Detergent solutions may also be used, but care must be taken to remove the detergent residue from the glassware. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants. Other approaches to cleaning glassware may also be employed, provided that the laboratory can demonstrate that they are effective in removing contaminants.

3.1.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations. One or more blanks should be run to check for cross-contamination.

3.1.3 After analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross contamination.

3.2 Matrix interferences may be caused by contaminants that are in the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. If significant interferences occur in subsequent samples, additional cleanup may be necessary.

4.0 APPARATUS AND MATERIALS

4.1 Macrodistillation System

4.1.1 Round bottom flask - 2-L, 14/20 ground-glass joint.

4.1.2 Vigreux column - 20 cm long, 14/20 ground-glass joint.

4.1.3 Modified Nielson-Kryger apparatus (Figure 1) - This glassware can be made by a glassblower, or a similar apparatus can be purchased and then modified by a glassblower according to the dimensions given in Figure 1.

4.1.4 Recirculating, submersible pumps - One for each distillation apparatus. Alternatively, a water chiller may be used in place of a recirculating submersible pump, with ice water, if the chiller can maintain a temperature of 0°C to 5°C in all distillation condensers.

4.1.5 Five-gallon container - Preferably insulated, holds ice water to maintain condenser temperature.

4.1.6 Volumetric glassware - 10-mL class A volumetric flasks and volumetric pipets of various sizes, 1 to 3 mL.

4.1.7 Sample/standard vials - 4-dram glass, with polytetrafluoroethylene (PTFE)-lined screw cap or crimp top vials.

4.1.8 pH Paper - narrow range (6.0-8.0).

4.2 Microdistillation System

4.2.1 Wadsworth MicroVOC System - Shamrock Glass, or equivalent.

4.2.1.1 Round bottom flask - 100-mL, 14/20 ground-glass joint.

4.2.1.2 Fractionation column - 14/20 ground-glass joint, 1.6 cm OD, 1.3 cm ID, 60 cm length (see Figure 2).

4.2.1.3 Pipe insulation - polyurethane foam, 1.5 inch OD, 0.5 inch ID, 55 cm in length.

4.2.1.4 Glass beads, 5 mm OD.

4.2.1.5 Keck clamps for 14/20 ground-glass joint.

4.2.1.6 Glass reducing union - 14/20 ground-glass joint to 6 mm OD tube (see Figure 3).

4.2.1.7 Stainless steel reducing union - 1/16 inch to 1/4 inch.

4.2.1.8 Air condenser - PTFE tubing, 1/16 inch OD to 1/32 inch ID (40 cm in length, or equivalent).

4.2.2 Support stand with rod - 1 meter.

4.2.3 Three-finger clamps.

4.2.4 Heating mantle - Glas-Col, 115 volts, 230 watts, STM 400, or equivalent.

4.2.5 Temperature controller - Glas-Col PL-115-Cordtrol, 115 volts, 600 watts, or equivalent.

4.2.6 Porous carbon boiling chips - VWR Catalog No. 26397-409, or equivalent.

4.2.7 Autosampler vials - glass, with PTFE-lined screw cap or top vials.

4.2.8 Autosampler vial inserts, 100-µL - The vial may be calibrated by dispensing a known volume of liquid into it, and marking the side of the vial.

4.3 Balance - Analytical, capable of weighing 0.0001 g.

4.4 Microsyringes - Various sizes.

5.0 REAGENTS

5.1 Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free Reagent Water - All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Potassium phosphate, monobasic, KH_2PO_4 (macrodistillation technique).

5.4 Sodium phosphate, dibasic, Na_2HPO_4 (macrodistillation technique).

5.5 Sodium chloride, NaCl (macrodistillation technique).

5.6 Stock Standard Solutions - Prepared from pure standard materials or from purchased certified solutions.

5.6.1 Prepare, in organic-free reagent water, a set of stock standard solutions each containing one of the target analytes. Place about 9.0 mL of organic-free reagent water in a 10 mL tared, ground-glass stoppered volumetric flask. Weigh the flask to the interest 0.0001 g. Add the assayed reference material, as described below:

5.6.1.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask using the known density as an approximate guide to place 0.100 g in the flask. The liquid must fall directly into the water without contacting the neck of the flask.

5.6.1.2 Solids - Add enough material to achieve approximately 0.100 g in the flask.

NOTE: The solubility of N-nitroso-di-n-butylamine in water is approximately 1000 mg/L. All other stock solutions should be 10,000 mg/L.

5.6.2 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.6.3 Transfer the stock standard solution into a PTFE-sealed screw cap bottle. Store, with minimal headspace, at 4°C, and protect from light.

5.6.4 Prepare fresh stock standard every month. Reactive compounds, such as acrylonitrile and N-nitroso-di-n-butylamine, may need to be prepared more frequently. Standards must be monitored closely. See individual determinative methods for calibration requirements.

5.7 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards, in organic-free reagent water, containing the compounds of interest, either singly or mixed together. Secondary dilution standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with minimal headspace in a refrigerator free of organic solvents. Standards should be monitored frequently and replaced when comparisons to independent check standards indicate a change of greater than 20%.

5.8 Stock Surrogate Solutions and Surrogate Spiking Solution

5.8.1 GC/MS Surrogates - Recommended surrogates for GC/MS analysis (Method 8260) include d_6-acetone, d_3-acetonitrile, d_3-methanol, d_5-pyridine, d_8-1,4-dioxane, and d_5-phenol. Although not all the analytes will have corresponding surrogates readily available, their use allows very accurate quantitation by isotope dilution methods. The stock surrogate

solutions should be prepared as in Sec. 5.6, and a surrogate spiking solution should be prepared from the stocks at a concentration so that addition of 50 µL of the spiking solution to the sample will produce a sample distillate with a concentration in the middle of the instrument calibration range, nominally 1000 mg/L. Each sample undergoing GC/MS analysis must be spiked with the spiking solution prior to distillation (nominal 50 µg added to the sample).

5.8.2 GC/FID Surrogates - Fluorinated alcohols and ketones may be used as surrogates when GC/FID analysis (Method 8015) is used, provided that the surrogates do not coelute with the target analytes. No single surrogate can be recommended, at present, when every compound listed in Sec. 1.1 is included in the analyte list. Nominally 50 µg of each fluorinated surrogate should be added to each sample prior to distillation.

NOTE: For small volume samples, the use of a spike volume greater than 200 µL may excessively dilute the sample and reduce analyte recovery.

5.9 Internal standards

5.9.1 GC/MS Internal Standards - The recommended internal standards when using GC/MS analysis (Method 8260) are d_{14}-diglyme (diethylene glycol dimethyl ether), d_6-isopropyl alcohol, d_7-dimethyl formamide, and d_5-benzyl alcohol. Other compounds may be used as internal standards provided they exhibit similar retention times to the compounds being detected. Care should be taken to avoid using compounds in which active hydrogens are deuterium labeled, as isotopic exchange would be expected in an aqueous matrix. The concentration of the secondary dilution standard and the spiking volume added to each distillate after distillation and just before GC/MS analysis should be consistent with the choice of a determinative method.

5.9.2 GC/FID Internal Standards - Halogenated alcohols, ketones, and nitriles may be used as internal standards when GC/FID analysis (Method 8015) is used. The recommended internal standards are hexafluoro-2-propanol, hexafluoro-2-methyl-2-propanol, and 2-chloroacetonitrile, however, these compounds may not be appropriate for all matrices. Nominally, 5 to 50 µg of each internal standard should be added to each sample prior to distillation. The total spike volume should be less than 1 mL to avoid excessive dilution of the sample and lower analyte recovery. However, the concentration of the secondary dilution standard and the spiking volume added to each prior to distillation should be consistent with the choice of a determinative method. Ethanol or other alcohols may be used as internal standards, provided that they are neither target analytes nor present in the sample.

5.10 Calibration standards

5.10.1 Prepare calibration standards using the recommended analyte, surrogate, and internal standard concentrations as specified in the appropriate determinative method (Methods 8015 or 8260). All calibration standards should be distilled by the same procedure as the samples for the microdistillation procedure.

5.11 All standards should be stored at 4°C in PTFE-lined, screw-capped vials with minimal headspace.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

NOTE: At this time, the effect of reducing agents or preservatives on method performance has not been evaluated. Preservation of samples is difficult because almost all preservatives could potentially interfere with the analysis. Storage at 4°C appears to be the best way to preserve most samples until analysis.

6.2 Samples should be analyzed within the designated holding time initiated at sample collection.

6.3 The distillate should be stored in a tightly sealed vial at 4°C in a refrigerator free of organic solvents. It is recommended that the distillate be analyzed within 24 hours of distillation. Distillates must be analyzed within 7 days of distillation.

7.0 PROCEDURE

7.1 Macrodistillation procedure

7.1.1 Set up the azeotropic distillation apparatus as shown in Figure 1. Fill the 5-gallon insulated container with ice and water, or connect the condenser to a chiller. It is very important to maintain a temperature of 0°C to 5°C in the condensers.

7.1.2 Measure a 1-L aliquot of sample with a 1000-mL graduated cylinder, and transfer it to a 1-L Erlenmeyer flask. Add 3.40 g KH_2PO_4, and 3.55 g Na_2HPO_4, and slowly stir with a stir bar and stir plate until dissolved. Check the pH with narrow range pH paper. The pH of the sample should be between 6.8 and 7.0. Add more Na_2HPO_4 if too acidic, or more KH_2PO_4 if too basic.

7.1.3 Transfer the buffered sample to a 2-L round-bottomed flask. Add 250 g of NaCl. Addition of salt has been shown to increase method efficiency for some of the compounds.

7.1.4 Spike the sample with 50 µL of the surrogate spiking solution (See Sec. 5.8).

7.1.5 Attach the Vigreux column to the flask and then the condenser.

7.1.6 Turn on the circulating pumps or chiller and heating mantles. After boiling has begun, the heating mantle voltage can be reduced approximately 10% to 15% to maintain an even boiling.

7.1.7 30 min after boiling begins, use a 5-mL syringe to remove the distillate from the reservoir and place it into a preweighed PTFE-lined screw cap vial. Take a second sample after an additional 30 minutes have elapsed and combine it with the first sample. Determine the weight of the distillate.

7.1.8 Add an amount of internal standard spiking solution so that the distillate will have a concentration of 10 mg/L. (For example, a 6-mL distillate would need 60 µg of internal standard). Mix well and store at 4°C until analysis.

7.2 Microdistillation procedure

7.2.1 Aqueous samples

7.2.1.1 Add 40 mL of the well-mixed sample to a 100-mL round-bottom flask. The sample volume should be the same volume used for the calibration standards. A smaller volume may be used if sample volume is limited, but the concentration factor will be reduced accordingly. If a smaller volume of sample is used, the analyst should add organic-free reagent water to the sample to make the volume approximately the same as that used for the standards and other samples.

Add approximately 0.14 g KH_2PO_4 and 0.14 g Na_2HPO_4, and slowly stir or swirl the sample until these buffering agents dissolve. Check the pH with narrow range pH paper. The pH of the sample should be between 6.8 and 7.0. Add more Na_2HPO_4 if too acidic, or more KH_2PO_4 if too basic.

7.2.1.2 Add appropriate volumes of the surrogate standards, internal standards and matrix spiking solutions.

7.2.1.3 Add 5 to 10 boiling chips to the flask, and place the flask in the heating mantle.

7.2.2 Solid samples

7.2.2.1 Add 5 g of sample to a 100-mL round bottom flask.

7.2.2.2 Add appropriate volumes of the surrogate standards, internal standards, and matrix spiking solutions.

7.2.2.3 Add 40 mL of organic-free reagent water to the flask, and place the flask in the heating mantle.

7.2.3 Assemble the micro distillation system (see Figure 4).

7.2.3.1 Attach the air condenser to the stainless steel reducing union (see Figure 3). The air condenser and reducing unions must be completely dry to avoid diluting or contaminating the distillate.

7.2.3.2 Fill the fractionation column with glass beads. The fractionation column and glass beads must be completely dry.

7.2.3.3 Insulate the column with polyurethane foam. Attach the fractionation column to the 100-mL round bottom flask. Adjust a three finger clamp to hold the column upright.

7.2.3.4 Attach the reducing union assembly to the top of the fractionation column, and hold in place with a Keck or three-finger clamp.

7.2.3.5 Place the free end of the air condenser into the collection vial.

7.2.4 Heat the sample at a rate sufficient to bring it to a boil in 2-4 minutes for water samples, and 3-5 minutes for solid samples. Using the heating mantle assembly described in Sec. 4.2.4, these rates correspond to settings of 75% and 60% on the rheostat, respectively.

7.2.5 Collect the first 100 to 300 µL of distillate in a calibrated microvial.

7.2.5.1 Some bubbles may be present in the condenser. This may make collecting exactly 100 µL difficult, but acceptable results can be obtained with practice.

NOTE: Once steam begins to condense at the top of the fractionation column, it normally takes less than 10 to 30 seconds for 100 µL of distillate to be collected.

7.2.5.2 As the distillate collects in the collection vial, slowly back the air condenser tube out of the micro-vial as it fills. This allows the bubbles to escape without dislodging the distillate from the micro-vial. Remove the free end of the condenser from the vial when the collected volume reaches 100 µL.

7.2.5.3 A larger volume of distillate may be collected by using a larger vial. In this case, the concentration factor will be reduced accordingly. Collecting a larger volume will require longer condensation times, and may require water cooling of the condenser. The steam flow rate continues to increase after the first 100 µL of distillate is produced. This flow can overwhelm the cooling capacity of the air condenser. Lengthening the condenser to 100 cm may also be helpful.

NOTE: When 100 µL of distillate is collected from a 40-mL or 5-g sample, the theoretical concentration factors are 400 and 50, respectively. Typical absolute recoveries of target analytes are 10% to 40%. Thus, the actual concentration factor is about 2 orders of magnitude for water samples and 1 order of magnitude for solid samples. Distilling all calibration standards compensates for low absolute recoveries.

7.2.6 Cap the collection vial and store at 4°C until the distillate is analyzed.

7.2.7 Turn off the heating mantle and allow the system to cool. Do not attempt to disassemble the apparatus while it is hot. Significant steam pressure has built up within the system during distillation. Disassembly could lead to a sudden release of steam. The use of a smaller ID condenser or higher heating rates is not recommended, since this may cause the steam within the system to reach an unsafe pressure.

7.3 Sample Analysis

7.3.1 The samples prepared by this method may be analyzed by the appropriate GC or GC/MS method, such as Methods 8015 and 8260. Refer to these methods for appropriate analysis conditions.

7.3.2 All distillates and standards must be allowed to warm to ambient temperature before analysis.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 To establish the ability to generate data of acceptable accuracy and precision refer to Method 8000 and the determinative method to be used.

9.0 METHOD PERFORMANCE

See Methods 8015 and 8260 for performance data.

10.0 REFERENCES

1. Peters, T.L. "Steam Distillation Apparatus for Concentration of Trace Water Soluble Organics"; Anal Chem., 1980, 52(1), 211-213.

2. Cramer, P.H., Wilner, J., and Stanley, J.S., "Final Report: Method for Polar, Water Soluble, Nonpurgeable Volatile Organics (VOCs)", For U.S. EPA, Environmental Monitoring Support Laboratory, EPA Contract No. 68-C8-0041.

3. Lee, R.P., Bruce, M.L., and Stephens, M.W., "Test Method Petition to Distill Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", submitted by Wadsworth/ALERT Laboratories Inc., N. Canton, OH, January, 1991.

4. Bruce, M.L., Lee, R.P., and Stephens, M.W., "Concentration of Water Soluble Volatile Organic Compounds from Aqueous Samples by Azeotropic Microdistillation", Environ. Sci. Technol., 1992, 26, 160-163.

11.0 SAFETY

The following target analytes are known or suspected to be human carcinogens: acrylonitrile and 1,4-dioxane. Pure standard materials and stock standard solutions of these compounds should be handled in a hood.

FIGURE 1
AZEOTROPIC MACRODISTILLATION SYSTEM

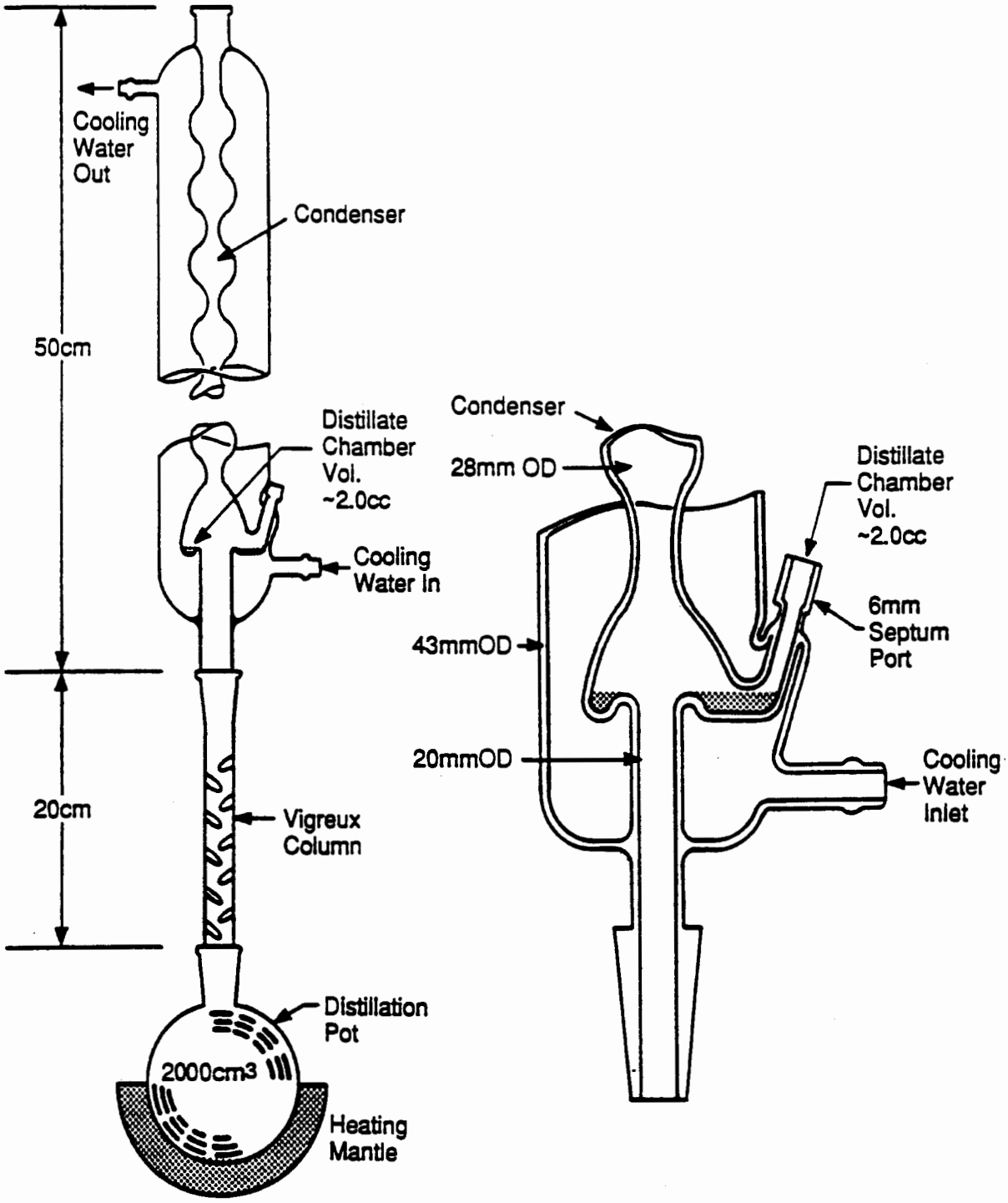


FIGURE 2
FRACTIONATION COLUMN

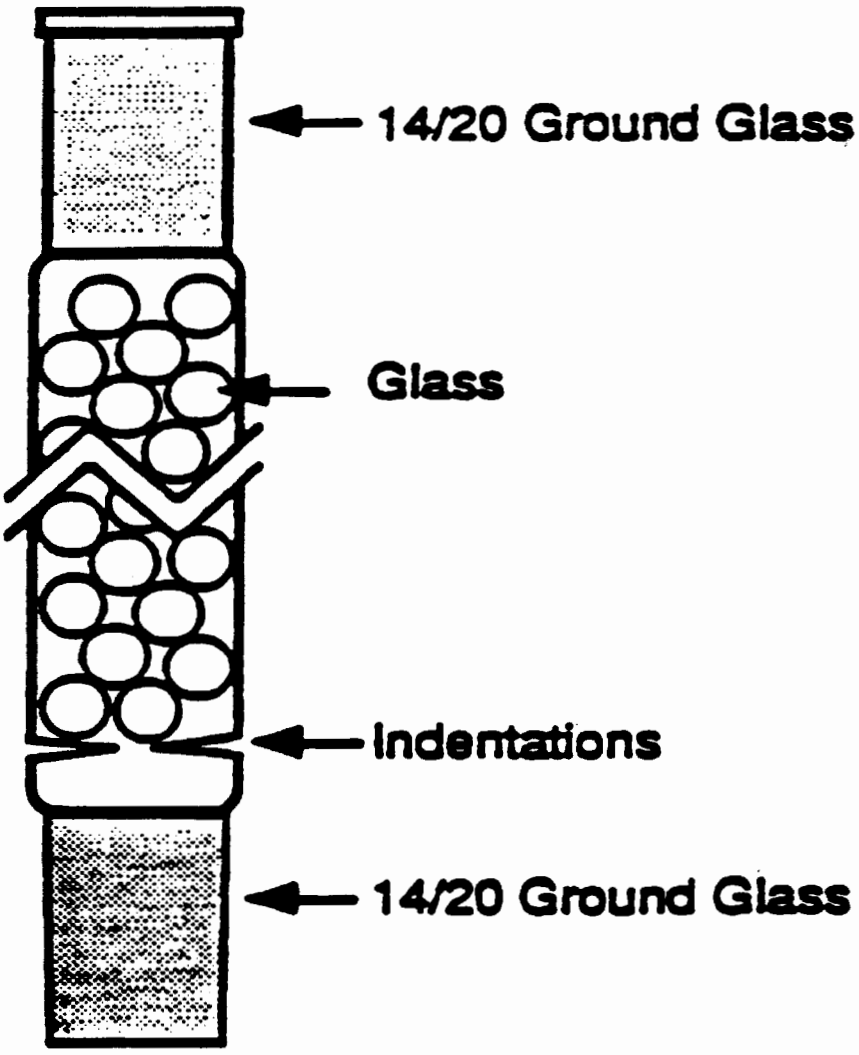


FIGURE 3
AIR CONDENSER AND REDUCING UNIONS

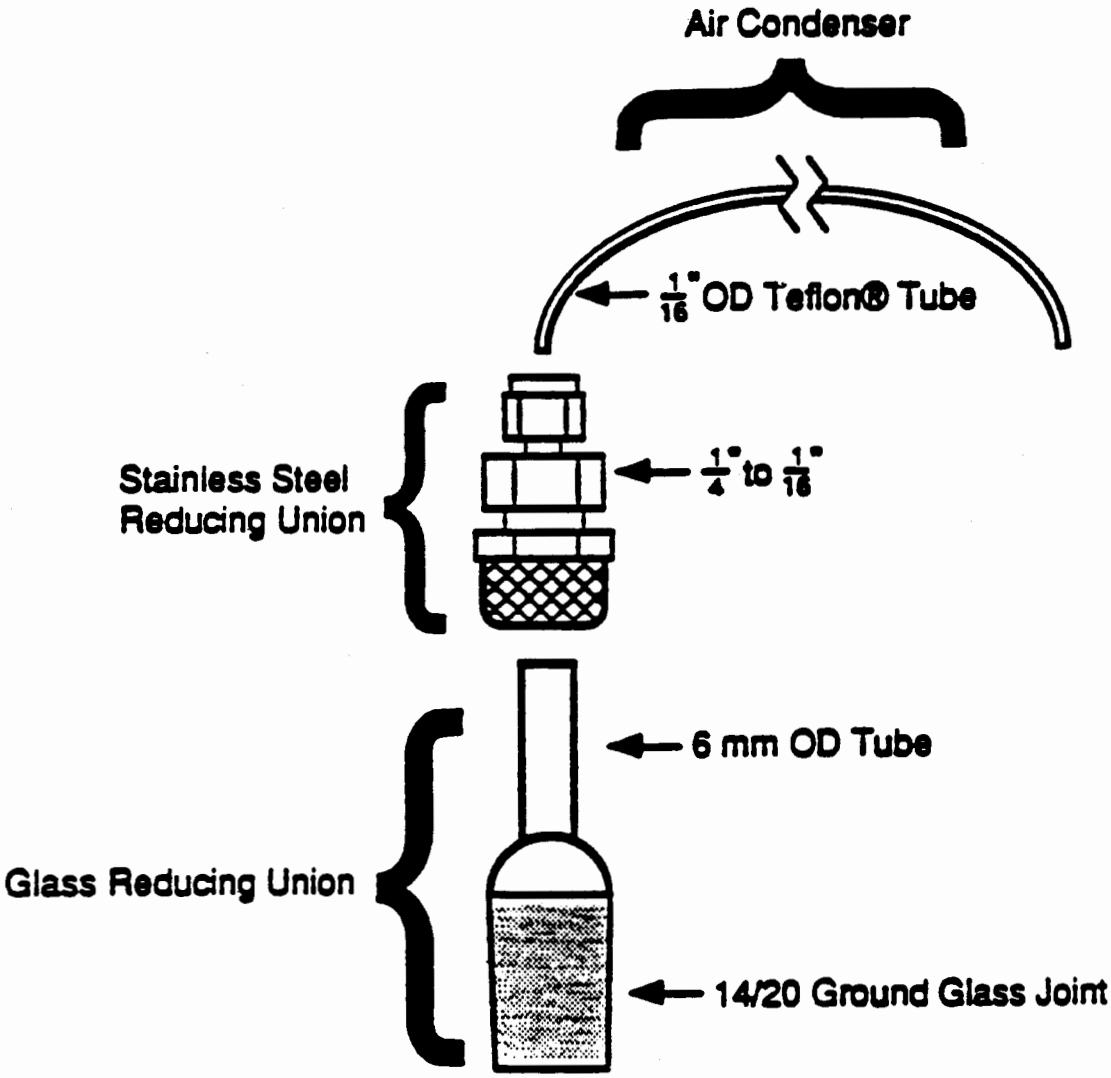
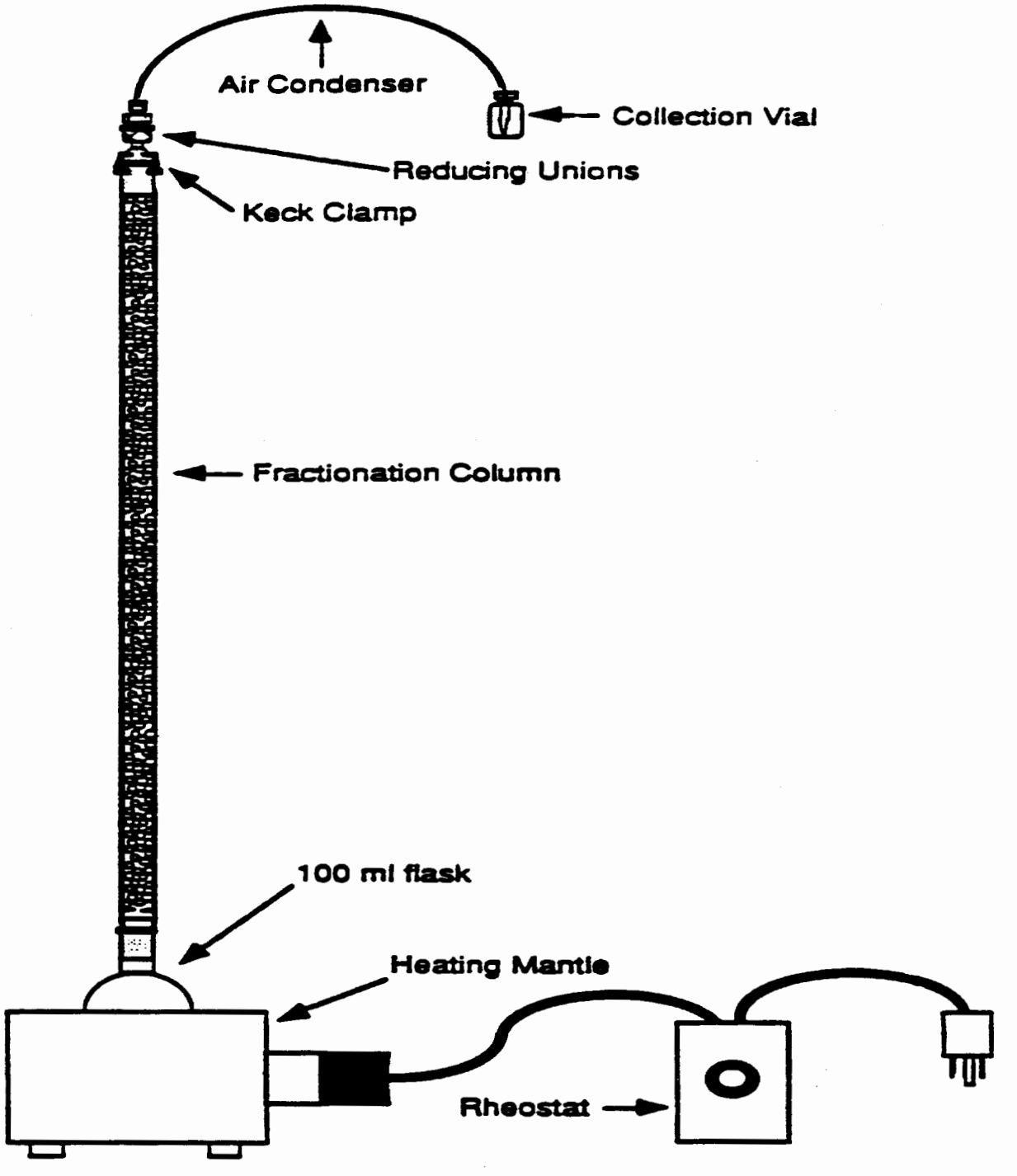
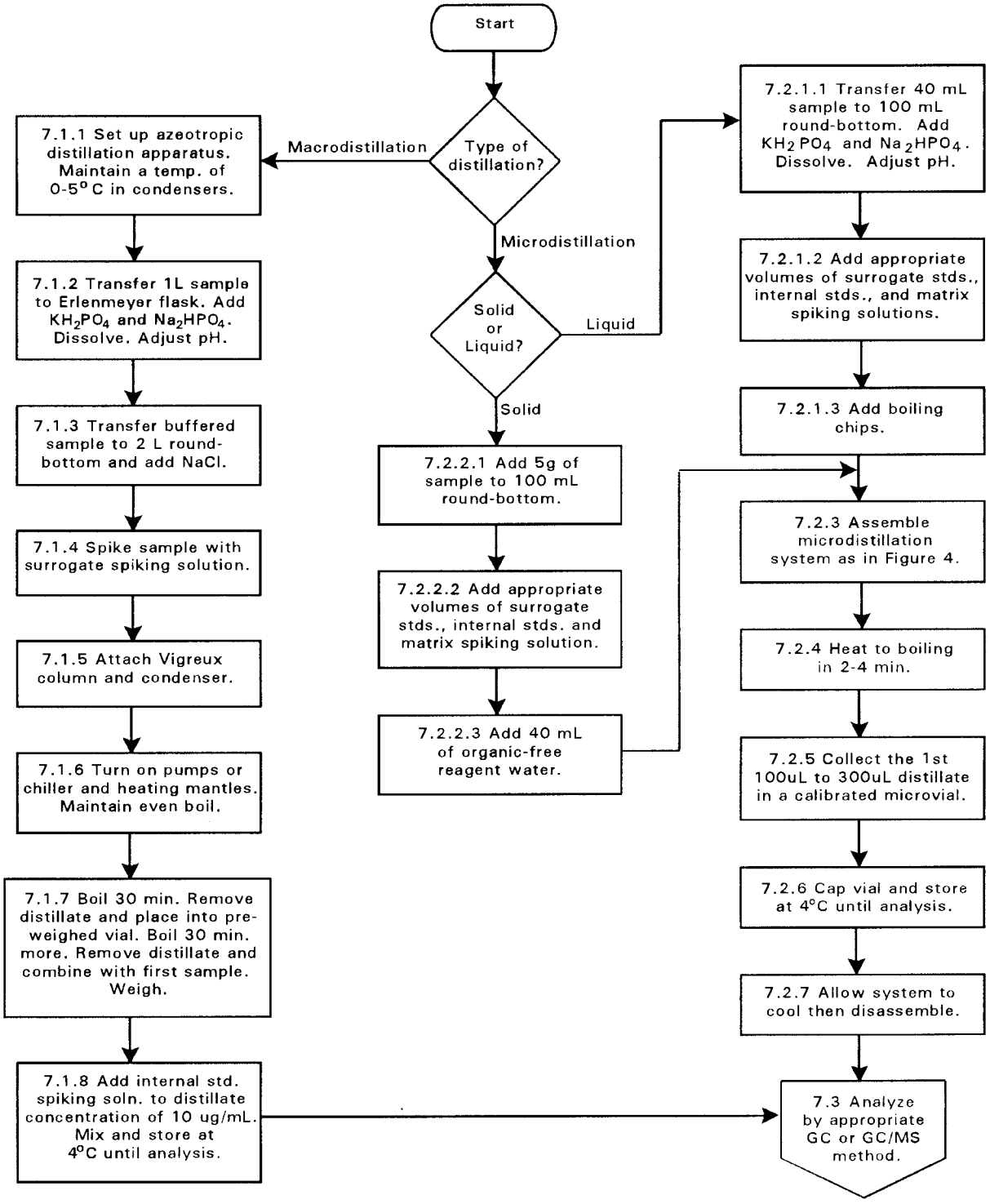


FIGURE 4
AZEOTROPIC MICRODISTILLATION SYSTEM




Start
Type of distillation?
Macrodistillation
Microdistillation
7.1.1 Set up azeotropic distillation apparatus. Maintain a temp. of 0-5°C in condensers.
7.1.2 Transfer 1L sample to Erlenmeyer flask. Add KH_2PO_4 and Na_2HPO_4. Dissolve. Adjust pH.
7.1.3 Transfer buffered sample to 2 L round-bottom and add NaCl.
7.1.4 Spike sample with surrogate spiking solution.
7.1.5 Attach Vigreux column and condenser.
7.1.6 Turn on pumps or chiller and heating mantles. Maintain even boil.
7.1.7 Boil 30 min. Remove distillate and place into pre-weighed vial. Boil 30 min. more. Remove distillate and combine with first sample. Weigh.
7.1.8 Add internal std. spiking soln. to distillate concentration of 10 ug/mL. Mix and store at 4°C until analysis.
Solid or Liquid?
Liquid
Solid
7.2.2.1 Add 5g of sample to 100 mL round-bottom.
7.2.2.2 Add appropriate volumes of surrogate stds., internal stds. and matrix spiking solution.
7.2.2.3 Add 40 mL of organic-free reagent water.
7.2.1.1 Transfer 40 mL sample to 100 mL round-bottom. Add KH_2PO_4 and Na_2HPO_4. Dissolve. Adjust pH.
7.2.1.2 Add appropriate volumes of surrogate stds., internal stds., and matrix spiking solutions.
7.2.1.3 Add boiling chips.
7.2.3 Assemble microdistillation system as in Figure 4.
7.2.4 Heat to boiling in 2-4 min.
7.2.5 Collect the 1st 100uL to 300uL distillate in a calibrated microvial.
7.2.6 Cap vial and store at 4°C until analysis.
7.2.7 Allow system to cool then disassemble.
7.3 Analyze by appropriate GC or GC/MS method.

VOLATILE ORGANIC COMPOUNDS BY VACUUM DISTILLATION

1.0 SCOPE AND APPLICATION

1.1 Method 5032 is used to determine volatile organic compounds in a variety of liquid, solid, oily waste matrices, and animal tissues. This method is applicable to nearly all types of matrices regardless of water, soil, sediment, sludge, oil, and biota content. Method 5032 is useful in the determination of the following compounds:

Compound Name	CAS No.[a]
Acetone	67-64-1
Acrolein	107-02-8
Acrylonitrile	107-13-1
Benzene	71-43-2
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
2-Butanone	78-93-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chlorodibromomethane	124-48-1
Chloroethane	75-00-3
2-Chloroethyl vinyl ether	110-75-8
Chloroform	67-66-3
Chloromethane	74-87-3
Dibromomethane	74-95-3
1,4-Dichloro-2-butene	764-41-0
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-35-4
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-3
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethanol	64-17-5
Ethylbenzene	100-41-4
Ethyl methacrylate	97-63-2
2-Hexanone	591-78-6
Iodomethane	74-88-4
Methylene chloride	75-09-2
4-Methyl-2-pentanone	108-10-1
Styrene	100-42-5
1,1,2,2-Tetrachloroethane	79-34-5

(continued)

Compound Name	CAS No.[a]
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane	96-18-4
Vinyl acetate	108-05-4
Vinyl chloride	75-00-3
m-Xylene	108-38-3
p-Xylene	106-42-3
o-Xylene	95-47-6

[a] Chemical Abstract Service Registry Number.

1.2 This method can be used to quantitate most volatile organic compounds that have a boiling point below 180°C and are insoluble or slightly soluble in water. Reference Method 8260 for a list of compounds, retention times, and their characteristic ions that have been evaluated on the vacuum distillation GC/MS system. Method 8260 also presents a list of compounds that represent a wide range of physical properties. These compounds have been minimally investigated to assist in identifying potential analytes of this method.

1.3 The method detection limits (MDL) determined are identified in tables located in Method 8260. Samples that require dilution will have proportionately higher detection limits.

1.4 Method 5032 is based on a vacuum distillation and cryogenic trapping procedure followed by gas chromatography/mass spectrometry. Alternate columns and detectors may be substituted when appropriate.

1.5 This method is restricted to use by, or under the supervision of, experienced personnel who are familiar with the techniques of vacuum distillation and experienced in the use of gas chromatographs and mass spectrometers as a quantitative tool. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The sample is introduced into a sample flask which is then attached to the apparatus (Figure 1). The sample chamber pressure is reduced using a vacuum pump and remains at approximately 10 torr (vapor pressure of water) as water is removed from the sample. The vapor is passed over a condenser coil chilled to a temperature of -10°C or less, which results in the condensation of water vapor. The uncondensed distillate is cryogenically trapped on a section of 1/8 inch stainless steel tubing chilled to the temperature of liquid nitrogen (-196°C). After an appropriate distillation period which may vary due to matrix or analyte group, the condensate

contained in the cryotrap is thermally desorbed and transferred to the gas chromatograph using helium carrier gas.

2.2 It is emphasized that the apparatus conditions are optimized to remove analyte from the sample matrix and isolate water from the distillate. The conditions may be varied to optimize the method for a given analyte or group of analytes. The length of time required for distillation may vary due to matrix effects or the analyte group of interest. Operating parameters may be varied to achieve optimum analyte recovery.

3.0 INTERFERENCES

3.1 Method interference may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baseline in the chromatograms.

3.1.1 Interferences distilled from the sample will vary from source to source, depending on the particular sample or matrix. The analytical system should be checked to insure freedom from interferences by analyzing method blanks under identical conditions of analysis.

3.1.2 The apparatus can be decontaminated with a ten minute evacuation of the distillation apparatus while the condenser coils are heated to 45^{o}C.

3.2 The laboratory where analysis is to be performed should be completely free of solvents. Many common solvents, most notably acetone and methylene chloride, are frequently found in laboratories at low levels. The sample receiving chamber should be loaded in a clean environment to eliminate this problem.

3.3 Samples may be contaminated during shipment. Field and trip blanks should be analyzed to insure integrity of the transported sample. It is recommended that wherever possible, samples aliquots and surrogates are transferred directly to sample flasks in the field, weighed and sealed using O-ring connections.

3.4 Impurities in purge gas and from organic compounds out-gassing from plumbing account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by including laboratory reagent blanks. All gas lines should be equipped with hydrocarbon and oxygen removal traps.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes: 10 µL, 25 µL, 100 µL, 250 µL, 500 µL, and 1000 µL. These syringes should be equipped with a 20 gauge (0.006 in. ID) needle.

4.2 Syringe: 5 mL and 10 mL gas tight, with Luer Lock tip and needles.

4.3 Balance: Analytical, capable of accurately weighing 0.0001 g, and a top loading balance capable of weighing 0.1 g.

4.4 Balance weights: Stainless steel S-class weights ranging from 5 mg to 100 g.

4.5 Sample Flask: 100 mL Pyrex® bulb joined to a 15 mm ID Pyrex® O-ring connector. The flask must be capable of being pumped down to a pressure of 10 mtorr without implosion. The flask is sealed for sample storage with a Buna-N O-ring, a 15 mm ID O-ring connector cap, and a pinch clamp.

4.6 Vacuum distillation apparatus (see Figure 1): The basic apparatus consists of a sample chamber connected to a condenser which is attached to a heated six port valve (V4). The sampling valve is connected to the following;

1) condenser (by way of Vacuum Pump Valve - V3)
2) vacuum pump
3) cryotrap
4) gas chromatograph/mass spectrometer

The sampling valve (V4) is heated to prevent condensation and potential carryover.

The circulating system which supplies the condenser coils consists of a cryogenic cooler with reservoir and an elevated temperature bath (45°C). The coolant reservoir may be filled with isopropyl alcohol or other appropriate fluid such as salt water. The fluid is circulated through the condenser coils with a peristaltic pump and the alternating of bath fluids are accomplished by the circulating fluid valve (V3).

The apparatus is heated to a temperature sufficient to prevent condensation of analytes onto condenser walls, valves, and connections. The temperature of the transfer line from the sampling valve to the gas chromatograph should be heated to the upper temperature utilized by the GC program.

Pirani gauges are recommended at the sample chamber, condenser and vacuum pump for distillation monitoring. Edwards Pirani gauge model 1001 with Pirani gauge head model PRH10K or equivalent.

The dimensions of the various parts of the apparatus are as follows:

1) The loop on which the sample is condensed is an 8 inch by 1/8 inch stainless steel piece of tubing.

2) The condenser is 12 inches long and 2 inches in diameter. The ends are made of ½ inch ground glass and are secured to all stainless steel joints by the use of ½ inch Buna rubber O-rings. The cooling coils within the condenser are made of 3/16 inch glass which terminate as 1/4 inch tubing fittings on the exterior of the condensers.

3) The cooling liquid passing through the condenser is routed from the refrigerant reservoir using 1/4 inch pure silicone tubing.

4) The tubing between the GC inlet and the six port valve is made of 1/16 inch capillary fused silica lined stainless steel.

5) The sampling chamber valve (V1) and the vacuum pump valve V3) are made of ½ inch stainless steel.

6) The circulating fluid valve (V2) is made of 1/4 inch brass.

7) The six port sampling valve (V4) is made of stainless steel with polytetrafluoroethylene (PTFE) internal parts.

4.7 Gas chromatograph/mass spectrometer system:

4.7.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.7.2 Column: 30 m by 0.7 mm ID fused silica capillary column chemically bonded with methylphenyl cyanopropyl silicone J&W DB-624, or equivalent, 3.0 µm film thickness.

4.7.3 Mass spectrometer: Capable of scanning from 35-350 amu every 2 sec. or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria listed in Method 8260 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.

4.7.4 Gas chromatograph/mass spectrometer heated jet separator interface: A heated glass jet separator interface capable of removing from 10 to 40 mL/min of helium from the exit end of the wide bore capillary column. The interface should have the ability to be heated through a range of 100 to 220°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol: CH_3OH, purge and trap grade or equivalent. Store apart from other solvents.

5.4 Standard solutions: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.4.1 Place about 9.8 mL of methanol in a 10 mL tared, ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.4.2 Add the assayed reference material, as described below.

5.4.2.1 Liquids: Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.4.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side-arm relief valve and direct a gentle stream of gas onto the methanol meniscus.

5.4.3 Reweigh, dilute to volume, stopper, and mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.4 Transfer the stock standard solution into a PTFE-sealed screw cap bottle. Store, with minimal headspace, at -10 to -20°C and protect from light.

5.4.5 Prepare fresh gas standards every two months. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Surrogate standards: The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Section 5.1, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 25 µg/mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis.

5.7 Internal Standards: It is recommended that one or more internal standards be selected from: bromochloromethane, 1,4-difluorobenzene, vinyl chloride-d_3, chlorobenzene-d . $_5$ The compound(s) selected should demonstrate minimal matrix effects. Other compounds maybe used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Method 8260 should be reviewed to select compounds appropriate for the matrix being tested. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.1 and 5.2. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 µg/mL of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L.

5.8 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 ng/µL of BFB in methanol should be prepared.

5.9 Calibration standards: Calibration standards at minimum of five concentration levels should be prepared from the secondary dilution of stock standards (see Secs. 5.1 and 5.2). Prepare these solutions in reagent water or purge and trap grade methanol. For each analyte, at least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project, which may include establishing compliance with a regulatory or action limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples and should not exceed the working range of the GC/MS system. Each standard should contain each analyte to be determined by this method (e.g., some or all of the compounds listed in Method 8260 may be included). Store for one week or less at -10°C in a vial with minimal headspace.

5.10 Matrix spiking standards: matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,2-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 25 µg/mL.

5.11 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards be stored at -10 to -20°C in screw-cap amber bottles with PTFE liners.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

6.2 Samples to be analyzed for volatile compounds should be stored separately from standards and other samples.

6.3 Holding times for oil and tissue samples have not been established. Tissue samples should be stored frozen (-20 °C) until analysis. Water and soil samples should be stored consistent with established procedures (see Chapter Two).

7.0 PROCEDURE

7.1 Recommended GC/MS operating conditions:

Electron energy:	70 volts (nominal)
Mass range:	35-350 amu
Scan time:	To give 8 scans/peak but not to exceed 3 sec/scan
Initial column temperature:	10°C
Initial hold time:	3.0 min
Column ramp rate:	5.0°C/min
Final column temperature:	230°C
Final hold time:	1.0 min

7.2 Initial calibration for vacuum distillation procedure:

7.2.1 Turn the six port sampling valve (V4) handle to the load position.

7.2.2 Place a styrofoam cup under the sample loop and secure in place. Fill the cup with liquid N_2. Recharge the styrofoam cup under the sample loop throughout the distillation with liquid N_2 as necessary.

7.2.3 Turn the sample chamber valve (V1) to the off position and remove the sample container.

7.2.4 Load the standard, containing surrogates and internal standards, into the sample flask and attach to the apparatus.

7.2.5 Turn the coolant/heat valve (V2) to circulate coolant through the condenser coils. Be sure all connections are complete and sealed properly. Open the sample chamber valve to begin the distillation. Continue distillation for 10 minutes.

NOTE: IF PIRANI GAUGES ARE USED: After five minutes of distillation the Pirani gauge at the vacuum pump should indicate about 0.1 torr, and the Pirani gauge at the condenser and should indicate 250 torr or less. After ten minutes of distillation the Pirani gauge at the sample chamber should read approximately 10 torr. If these pressures are not attained a leak may be present and the distillation may not be successful. Distillation performance surrogates should be evaluated for acceptability of distillation.

7.2.6 Setup the data system for acquisition of the data file. This may be done prior to the beginning of step 1. While distillation times may be variable depending on sample matrix, the data system should be ready and the GC oven at equilibrium by the time the distillation is complete.

7.2.7 Once the distillation is complete GC/MS analyses may be performed. Turn the sampling valve handle to the inject position while maintaining the styrofoam cup with liquid N_2 in place. Rapidly remove the styrofoam cup and replace with the beaker of (90°C) hot tap water and commence GC/MS data acquisition.

7.2.8 Once acquisition has begun the sample chamber valve may be closed and the sample flask removed.

7.2.9 The distillation apparatus can then be readied for the next analyses. This is performed by switching the vacuum pump valve (V3) to the vacuum pump position which disconnects the vacuum stream to the sampling valve (V4). The condenser circulating fluid is then switched to the heated fluid (45°C) by switching valve V2. Evacuate the distillation system for 10 minutes. It is recommended that a liquid nitrogen cooling trap be placed between valve V3 and the vacuum pump to prevent degradation of the vacuum due to overload of moisture in the vacuum pump oil.

7.3 Calibration response factors: Calculate according to Method 8260.

7.4 Sample preparation:

7.4.1 Liquid samples should be stored with minimal or no headspace to minimize the loss of more volatile analytes. Aqueous samples may be preserved with ascorbic acid to stop biological degradation which may occur in water samples. The recommended sample size for water is 5 mL. Other sample sizes may be employed, provided that the sensitivity is adequate to meet the project objectives.

7.4.2 Solid and soil samples should be rapidly withdrawn from their sample container and weighed while still cold. The sample is then rapidly transferred to the sample chamber and secured to prevent loss of analytes. The recommended sample size for solid samples is 5 g. Other sample sizes may be employed, provided that the sensitivity is adequate to meet the project objectives.

7.4.3 Tissue samples which are fleshy may have to be minced into smaller pieces to get them through the neck of the sample chamber. This is best accomplished by freezing the sample in liquid nitrogen before any additional processing takes place. Biota samples containing leaves and other softer samples may be minced using clean scissors. The sample size is a function of the sensitivity necessary to meet the project objectives. Samples as large as 10 g can be analyzed with this method, but smaller samples may be more appropriate.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is analyzed, or there is a change in reagents, a method blank should be processed as a safeguard against laboratory contamination. The blank samples should be carried through all stages of sample preparation and measurement.

8.3 To establish the ability to generate data of acceptable accuracy and precision refer to Method 8000 and the determinative method to be used.

8.4 Matrix and distillation performance surrogates.

8.4.1 Matrix effects and distillation performance may be monitored separately through the use of surrogates. Compounds that have demonstrated minimal matrix effects such as vinyl chloride-d_3 and bromochloromethane may be added directly to the matrix and used as an internal standard. Tables located in Method 8260 present recovery data from water, soil and oil matrices that should be considered when selecting surrogates. Compounds that have demonstrated matrix effects and/or distillation losses (i.e., pyridine-d_5, 2-fluorophenol for matrix effects and 1,2-dichlorobenzene-d_4 for distillation performance) are recommended as surrogates.

8.4.2 The use of multiple matrix surrogates and multiple distillation performance surrogates are recommended. It is recommended that distillation effect surrogates be relatively insoluble in water. Matrix monitoring compounds should be selected to bracket the physical properties of the analytes of interest. If matrix effects have been shown or are suspected for a chosen distillation surrogate compound, the distillation surrogates should be added to the sample flask in an open mini-vial suspended above the sample by a wire stand. Multiple surrogates for monitoring one or more classes of compounds are recommended for evaluating matrix effects.

8.5 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the

sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect <1 µg/g of the analytes in the sample, then the sensitivity of the instrument should be increased, or a larger amount of the sample should be used.

9.0 METHOD PERFORMANCE

9.1 Performance data for Method 5032 are provided in tables in Method 8260.

10.0 REFERENCES

1. Hiatt, M.H. "Analysis of Fish and Sediment For Volatile Priority Pollutants", Analytical Chemistry 1981, 53 (9), 1541.

2. Hiatt, M.H. "Determination of Volatile Organic Compounds in Fish Samples by Vacuum Distillation and Fused Silica Capillary Gas Chromatography/Mass Spectrometry"; Analytical Chemistry 1983, 55 (3), 506.

3. United States Patent 4,600,559. "Vacuum Extractor with Cryogenic Concentration and Capillary Interface", held by the U.S. EPA.

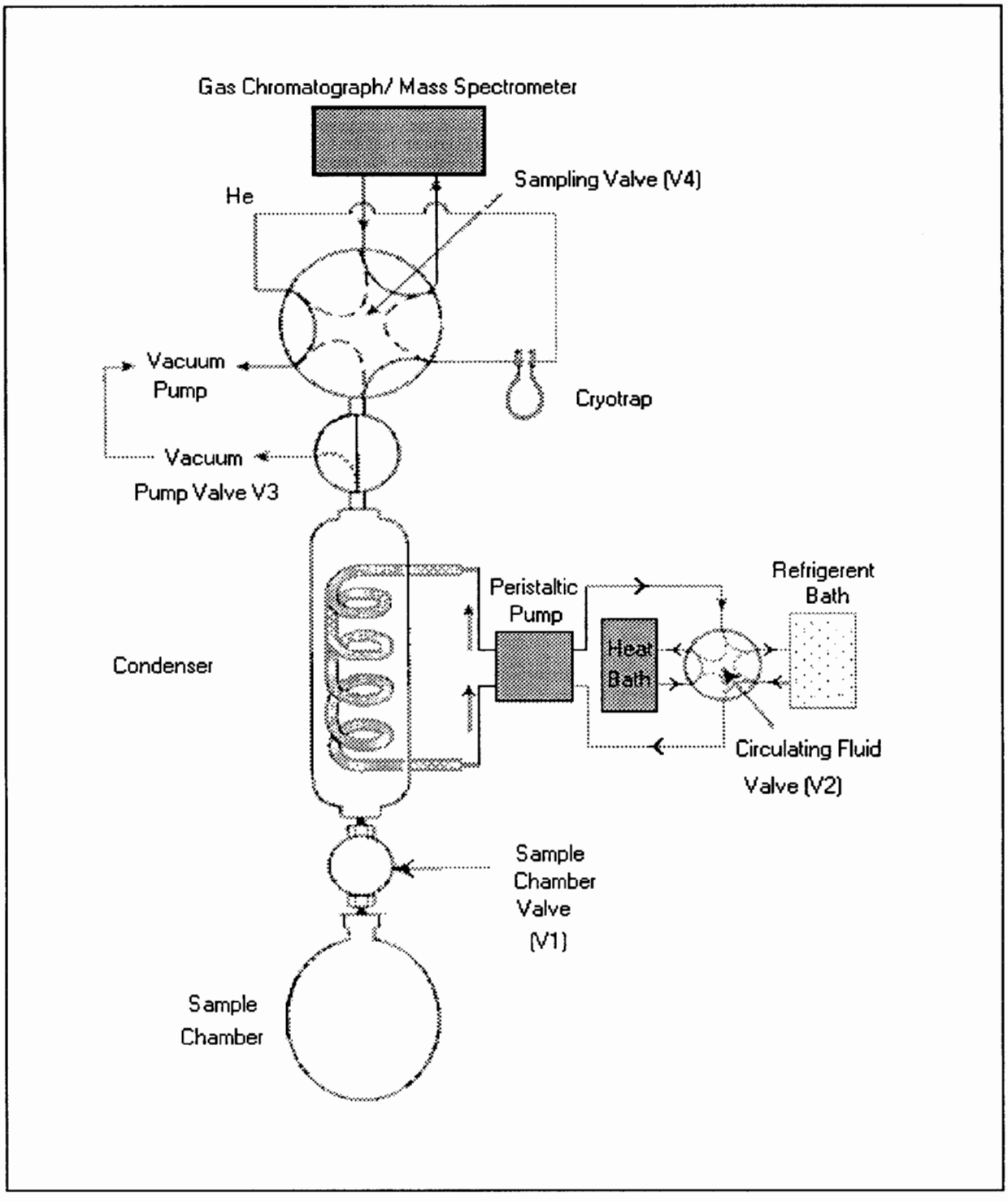
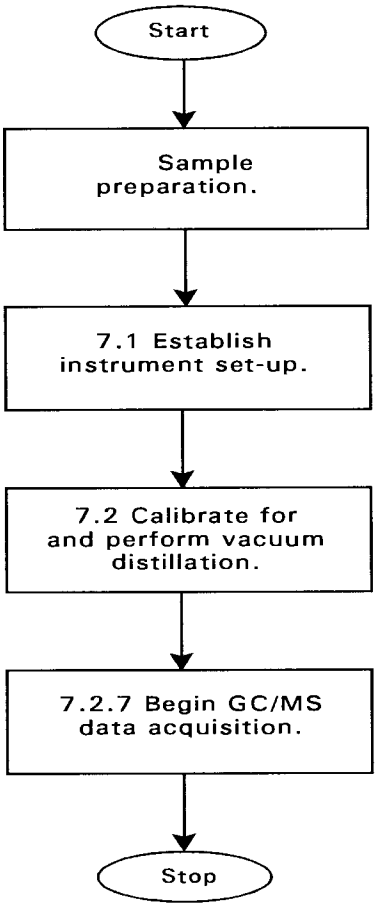


Figure 1
Vacuum Distillation Configuration

VOLATILE ORGANIC COMPOUNDS BY VACUUM DISTILLATION



METHOD 5035

CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

1.2 The low soil method utilizes a hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 0.5 to 200 µg/kg range.

1.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

1.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030..

1.5 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency.

1.6 Method 5035, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5035 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Method 8021 in series with Method 8015.

1.7 As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.8 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 6.2.2).

1.9 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to and soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains 5 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent.

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol or polyethylene glycol (PEG), a separate aliquot of the sample is spiked with surrogates and diluted in the appropriate solvent. An aliquot of the solution is added to 5 mL of reagent water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) are added to the solution which is then purged using Method 5030 and analyzed by an appropriate determinative method.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other

systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 4.2.2).

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the Disclaimer at the front of this manual for guidance on the use of alternative equipment.

4.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed, it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all the target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocarb 4000), as some degradation has been noted when higher desorption temperatures (especially above 240 - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 The trap used to develop this method was 25 cm long, with an inside diameter of 0.105 inches, and was packed with Carbopack/Carbosieve (Supelco, Inc.).

4.2.2.2 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If

the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

4.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.2.2.2.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.2.2.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.3 Syringe and Syringe Valves

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25-µL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10-, 100-µL.

4.3.5 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

4.4 Miscellaneous

4.4.1 Glass vials

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance - Capable of accurately weighing to 0.01 g.

4.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground-glass stoppers.

4.4.5 2-mL glass vials, for GC autosampler - Used for oily waste samples extracted with methanol or PEG.

4.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

4.5 Field Sampling Equipment

4.5.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.5.2 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.3 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

4.5.4 Portable balance - For field use, capable of weighing to 0.01 g.

4.5.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH_3OH - purge-and-trap quality or equivalent. Store away from other solvents.

5.3 Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$ - free of interferences at the detection limit of the target analytes.

5.4 Low concentration sample preservative

5.4.1 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

5.4.2 The preservative should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

5.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of ≤ 2.

6.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

6.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the

laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

6.1.2 High concentration soil samples collected without a preservative

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60-mL glass vials with septum seals (see Sec. 4.4).

6.1.3 High concentration soil samples collected and preserved in the field

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.3.1 Add 10 mL of methanol to each vial.

6.1.3.2 Seal the vial with the screw-cap and septum seal.

6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

NOTE: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

6.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the sample after it is returned to the laboratory and prior to analysis.

6.1.4 Oily waste samples

When oily waste samples are known to be soluble in methanol or PEG, sample vials may be prepared as described in Sec. 6.1.3, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 6.1.2.

6.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler ™, and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.2.1 Low concentration soil samples

6.2.1.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

NOTE: Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials that do not contain the preservative solution.

6.2.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

6.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60-mL glass vial or a third 40-mL soil sample vial. However, this third vial must *not* contain the sample preservative solution, as an aliquot will be used to determine dry weight. If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

6.2.1.7 If samples are known or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2 g instead of the 5 g collected in Sec. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

6.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 6.2.2).

6.2.2 High concentration soil samples preserved in the field

The collection of soil samples in vials that contain methanol has been suggested by some as a combined preservation and extraction procedure. However, this procedure is not appropriate for use with the low concentration soil procedure described in this method.

NOTE: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of two potential problems. First, the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure (0.5-200 µg/kg). The exact dilution factor will depend on the masses of solvent and sample, but generally exceeds 1000, and may make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes. Because the analytes of interest are volatile, the methanol extract cannot be concentrated to overcome the dilution problem. Thus, for samples of unknown composition, it may still be necessary to collect an aliquot for analysis by this closed-system procedure and another aliquot preserved in methanol and analyzed by other procedures. The second problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste.

6.2.2.1 When samples are known to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

6.2.2.2 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.2.3 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

6.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight, as described in Sec. 6.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

6.2.3 High concentration soil sample not preserved in the field

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

6.2.4 Oily waste samples

The collection procedures for oily samples depend on knowledge of the waste and its solubility in methanol or other solvents.

6.2.4.1 When an oily waste is known to be soluble in methanol or PEG, the sample may be collected in a vial containing such a solvent (see Sec. 6.1.4), using procedures similar to those described in Sec. 6.2.2.

6.2.4.2 When the solubility of the oily waste is not known, the sample should either be collected in a vial without a preservative, as described in Sec. 6.2.3, or the solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in Sec. 6.2.2. Otherwise, collect an unpreserved sample as described in Sec. 6.2.3.

6.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

6.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at -10°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel. See Sec. 6.2.1.2 for additional information.

7.0 PROCEDURE

This section describes procedures for sample screening, the low concentration soil method, the high concentration soil method, and the procedure for oily waste samples. High concentration samples are to be introduced into the GC system using Method 5030. Oily waste samples are to be introduced into the GC system using Method 5030 if they are soluble in a water-miscible solvent, or using Method 3585 if they are not.

7.1 Sample screening

7.1.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system**,** thereby requiring extensive cleanup and instrument maintenance. The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low concentration closed-system direct purge-and-trap method (Sec. 7.2), the high concentration (methanol extraction) method (Sec. 7.3), or the nonaqueous liquid (oily waste) methanol or PEG dilution procedure (Sec. 7.4).

7.1.2 The analyst may employ any appropriate screening technique. Two suggested screening techniques employing SW-846 methods are:

7.1.2.1 Automated headspace (Method 5021) using a gas chromatograph (GC) equipped with a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series, or,

7.1.2.2 Extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC equipped with a FID and/or an ECD.

7.1.3 The analyst may inject a calibration standard containing the analytes of interest at a concentration equivalent to the upper limit of the calibration range of the low concentration soil method. The results from this standard may be used to determine when the screening results approach the upper limit of the low concentration soil method. There are no linearity or other performance criteria associated with the injection of such a standard, and other approaches may be employed to estimate sample concentrations.

7.1.4 Use the low concentration closed-system purge-and-trap method (Sec. 7.2) if the estimated concentration from the screening procedure falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range of the low concentration soil method, then use either the high concentration soil method (Sec. 7.3), or the oily waste method (Sec. 7.4).

7.2 Low concentration soil method (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.2.1 Initial calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.2.1.2 Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing with an inert gas flow of at least 20 mL/minute. If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.3 If the standard trap in Sec. 4.2.2.2 is employed, prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min, or according to the manufacturer's recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.4 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

7.2.1.5 Prepare a minimum of five initial calibration standards containing all the analytes of interest and surrogates, as described in Method 8000, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL added to the vial before shipping it to the field plus the organic-free reagent water added by the instrument). The calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (e.g., ~1 g), as the presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same fashion as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the surrogates using standards at five concentrations, it may be necessary to disable the automatic addition of surrogates to each vial containing a calibration standard (consult the manufacturer's instructions). Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as recommended by the manufacturer.

7.2.1.6 Carry out the purge-and-trap procedure as outlined in Secs. 7.2.3. to 7.2.5.

7.2.1.7 Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.

7.2.1.8 For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.8.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.2.1.8.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.8.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.9 When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross-contamination and memory effects from a high concentration sample or even the standard are a common problem.

Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification

Refer to Method 8000 for details on calibration verification. A single standard near the mid-point of calibration range is used for verification. This standard should also contain approximately 1 g of sodium bisulfate.

7.2.3 Sample purge-and-trap

This method is designed for a 5-g sample size, but smaller sample sizes may be used. Consult the instrument manufacturer's instructions regarding larger sample sizes, in order to avoid clogging of the purging apparatus. The soil vial is hermetically sealed at the sampling site, and MUST remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01 g, even if the sample weight was determined in the field, and record this weight. This second weighing provides a check on the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant discrepancies between the field and laboratory weights.

7.2.3.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

7.2.3.2 Without disturbing the hermetic seal on the sample vial, add 5 mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

7.2.3.3 For the sample selected for matrix spiking, add the matrix spiking solution described in Sec. 5.0 of Method 5000, either manually, or automatically, following the manufacturer's instructions. The concentration of the spiking solution and the amount added should be established as described in Sec. 8.0 of Method 8000.

7.2.3.4 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

7.2.4 Sample Desorption

7.2.4.1 Non-cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow

of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes (1.5 min is normally adequate for analytes in Method 8015). Begin the temperature program of the gas chromatograph and start data acquisition.

7.2.4.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 245°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Methods 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.5 Trap Reconditioning

After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

7.2.6 Data Interpretation

Perform qualitative and quantitative analysis following the guidance given in the determinative method and Method 8000. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. Such reanalyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method. Alternatively, if a sample aliquot of 1-2 g was also collected (see Sec. 6.2.1.7), it may be practical to analyze that aliquot for the analytes that exceeded the instrument calibration range in the 5-g analysis. If results are to be reported on a dry weight basis, proceed to Sec. 7.5

7.3 High concentration method for soil samples with concentrations generally greater than 200 µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free reagent water containing surrogates and, if applicable, internal and matrix spiking standards, purged according to Method 5030, and analyzed by an appropriate determinative method. Wastes that are insoluble in methanol (i.e., petroleum and coke wastes) are diluted with hexadecane (see Sec. 7.3.8).

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were <u>not</u> preserved in the field are prepared using the steps below, beginning at Sec. 7.3.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.3.4.

7.3.1 When the high concentration sample is <u>not</u> preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Whenever practical, mix the contents of the sample container by shaking or other mechanical means without opening the vial. When shaking is not practical, quickly mix the contents of the vial with a narrow metal spatula and immediately reseal the vial.

7.3.2 If the sample is from an unknown source, perform a solubility test before proceeding. Remove several grams of material from the sample container. Quickly reseal the container to minimize the loss of volatiles. Weigh 1-g aliquots of the sample into several test tubes or other suitable containers. Add 10 mL of methanol to the first tube, 10 mL of PEG to the second, and 10 mL of hexadecane to the third. Swirl the sample and determine if it is soluble in the solvent. Once the solubility has been evaluated, discard these test solutions. If the sample is soluble in either methanol or PEG, proceed with Sec. 7.3.3. If the sample is only soluble in hexadecane, proceed with Sec. 7.3.8.

7.3.3 For soil and solid waste samples that are soluble in methanol, add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution to a tared 20-mL vial. Using a top-loading balance, weigh 5 g (wet weight) of sample into the vial. Quickly cap the vial and reweigh the vial. Record the weight to 0.1 g. Shake the vial for 2 min. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0 mL of PEG in place of the methanol. Proceed with Sec. 7.3.5.

NOTE: The steps in Secs. 7.3.1, 7.3.2, and 7.3.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.4 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 6.2.2), weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum, shake for 2 min, as described above, and proceed with Sec. 7.3.5.

7.3.5 Pipet approximately 1 mL of the extract from either Sec. 7.3.3 or 7.3.4 into a GC vial for storage, using a disposable pipet, and seal the vial. The remainder of the extract may be discarded. Add approximately 1 mL of methanol or PEG to a separate GC vial for use as the method blank for each set of samples extracted with the same solvent.

7.3.6 The extracts must be stored at 4°C in the dark, prior to analysis. Add an appropriate aliquot of the extract (see Table 2) to 5.0 mL of organic-free reagent water and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging high concentration samples.

7.3.7 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the procedure in Sec. 7.5, after the sample extract has been transferred to a GC vial and the vial sealed.

7.3.8 For solids that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste) dilute or extract the sample with hexadecane using the procedures in Sec. 7.0 of Method 3585.

7.4 High concentration method for oily waste samples

This procedure for the analysis of oily waste samples involves the dilution of the sample in methanol or PEG. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. A portion of the diluted sample is then added to 5.0 mL of organic-free reagent water, purged according to Method 5030, and analyzed using an appropriate determinative method.

For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with hexadecane using the procedures in Sec. 7.0 of Method 3585.

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.4.1. If methanol preservation was employed in the field, then the preparation begins with Sec. 7.4.3.

7.4.1 If the waste was not preserved in the field and it is soluble in methanol or PEG, weigh 1 g (wet weight) of the sample into a tared 10-mL volumetric flask, a tared scintillation vial, or a tared culture tube. If a vial or tube is used instead of a volumetric flask, it must be calibrated prior to use. This operation must be performed prior to opening the sample vial and weighing out the aliquot for analysis.

7.4.1.1 To calibrate the vessel, pipet 10.0 mL of methanol or PEG into the vial or tube and mark the bottom of the meniscus.

7.4.1.2 Discard this solvent, and proceed with weighing out the 1-g sample aliquot.

7.4.2 Quickly add 1.0 mL of surrogate spiking solution to the flask, vial, or tube, and dilute to 10.0 mL with the appropriate solvent (methanol or PEG). Swirl the vial to mix the contents and then shake vigorously for 2 minutes.

7.4.3 If the sample was collected in the field in a vial containing methanol or PEG, weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum. Swirl the vial to mix the contents and then shake vigorously for 2 minutes and proceed with Sec. 7.4.4.

7.4.4 Regardless of how the sample was collected, the target analytes are extracted into the solvent along with the majority of the oily waste (i.e., some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

7.4.5 Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis, using Method 5030.

7.4.6 Prepare a matrix spike sample by adding 10 - 50 µL of the matrix spike standard dissolved in methanol to a 1-g aliquot of the oily waste. Shake the vial to disperse the matrix spike solution throughout the oil. Then add 10 mL of extraction solvent and proceed with the extraction and analysis, as described in Secs. 7.4.2 - 7.4.5. Calculate the recovery of the spiked analytes as described in Method 8000. If the recovery is not within the acceptance limits for the application, use the hexadecane dilution technique in Sec. 7.0 of Method 3585.

7.5 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample.

NOTE: It is highly recommended that the dry weight determination only be made after the analyst has determined that no sample aliquots will be taken from the 60-mL vial for high

concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the dry weight determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

7.5.1 Weigh 5-10 g of the sample from the 60-mL VOA vial into a tared crucible.

7.5.2 Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS), and the addition of surrogates to each sample and QC sample.

8.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Single laboratory accuracy and precision data were obtained for the method analytes in three soil matrices, sand, a soil collected 10 feet below the surface of a hazardous landfill, called the

C-Horizon, and a surface garden soil. Each sample was fortified with the analytes at a concentration of 20 ng/5 g, which is equivalent to 4 µg/kg. These data are listed in tables found in Method 8260.

9.2 Single laboratory accuracy and precision data were obtained for certain method analytes when extracting oily liquid using methanol as the extraction solvent. The data are presented in a table in Method 8260. The compounds were spiked into three portions of an oily liquid (taken from a waste site) following the procedure for matrix spiking described in Sec. 7.4. This represents a worst case set of data based on recovery data from many sources of oily liquid.

10.0 REFERENCES

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TABLE 1

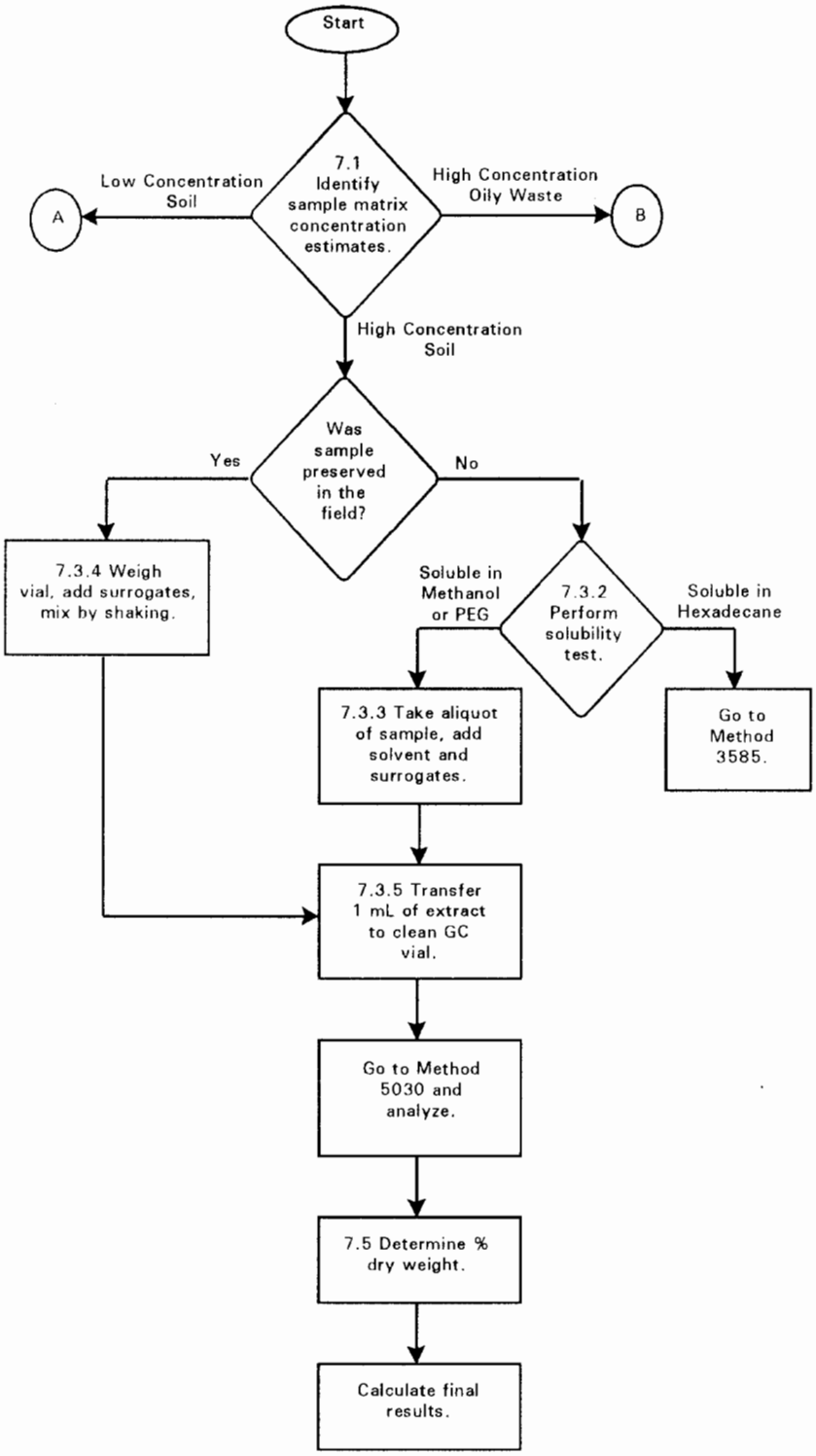
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SOILS/SEDIMENTS

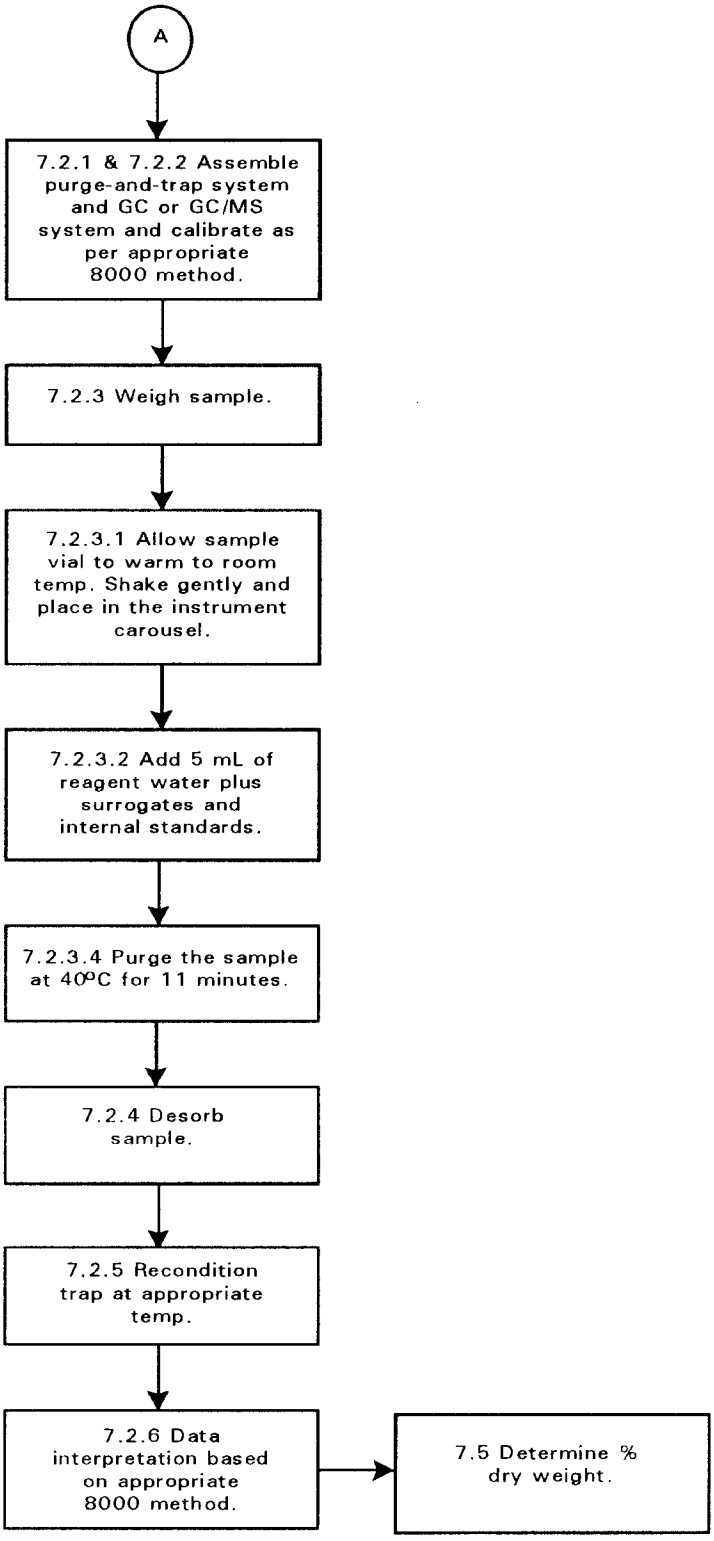
Approximate Concentration Range	Volume of Methanol Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

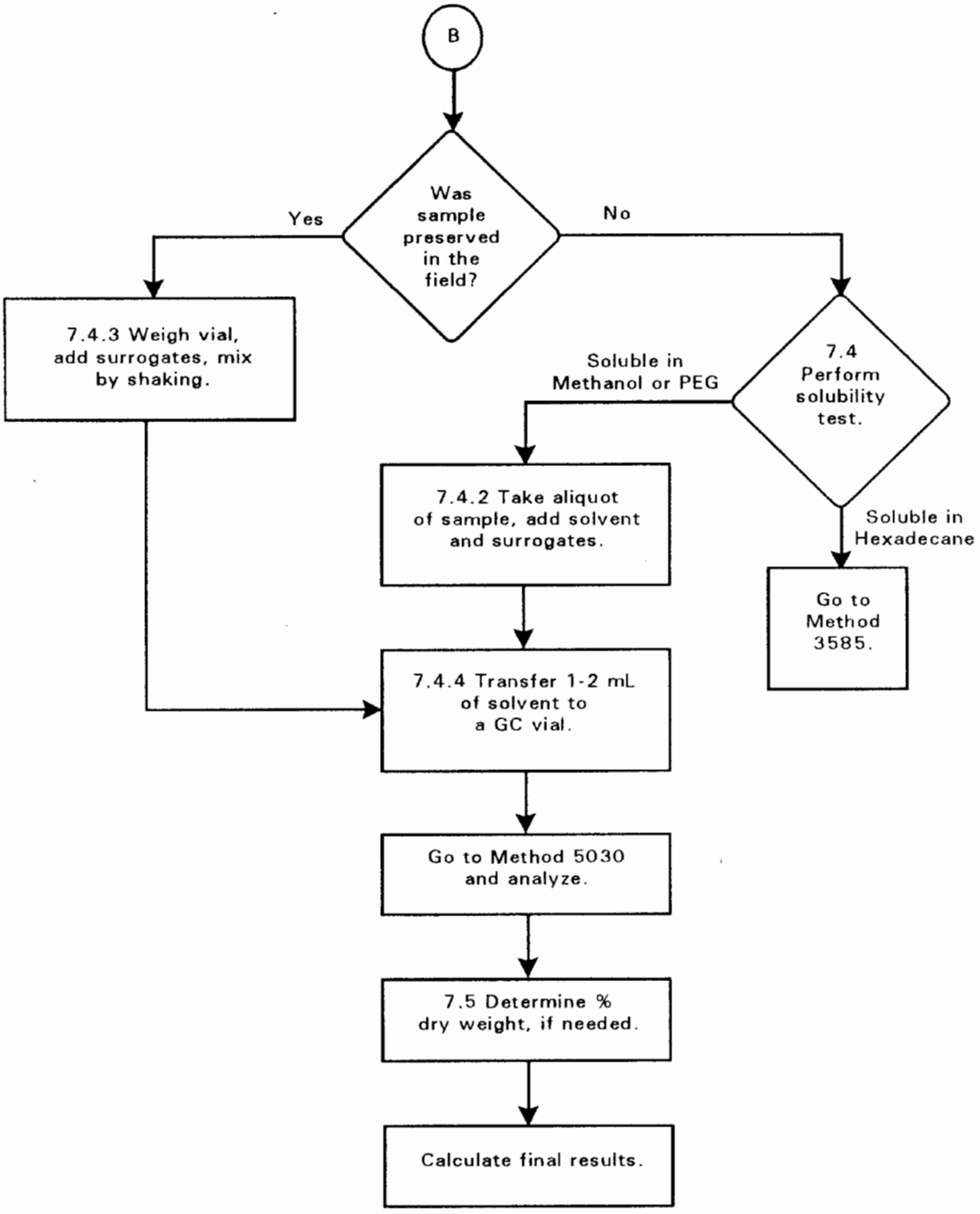
Calculate appropriate dilution factor for concentrations exceeding those in this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100 µL of methanol.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.


Start
7.1 Identify sample matrix concentration estimates.
Low Concentration Soil
A
High Concentration Oily Waste
B
High Concentration Soil
Was sample preserved in the field?
Yes
No
7.3.4 Weigh vial, add surrogates, mix by shaking.
7.3.2 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.3.3 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.3.5 Transfer 1 mL of extract to clean GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight.
Calculate final results.


A
7.2.1 & 7.2.2 Assemble purge-and-trap system and GC or GC/MS system and calibrate as per appropriate 8000 method.
7.2.3 Weigh sample.
7.2.3.1 Allow sample vial to warm to room temp. Shake gently and place in the instrument carousel.
7.2.3.2 Add 5 mL of reagent water plus surrogates and internal standards.
7.2.3.4 Purge the sample at 40°C for 11 minutes.
7.2.4 Desorb sample.
7.2.5 Recondition trap at appropriate temp.
7.2.6 Data interpretation based on appropriate 8000 method.
7.5 Determine % dry weight.


B
Was sample preserved in the field?
Yes
No
7.4.3 Weigh vial, add surrogates, mix by shaking.
7.4 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.4.2 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.4.4 Transfer 1-2 mL of solvent to a GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight, if needed.
Calculate final results.

METHOD 5041A

ANALYSIS FOR DESORPTION OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN (VOST)

1.0 SCOPE AND APPLICATION

1.1 This method describes the desorption of volatile principal organic hazardous constituents (POHCs) collected from the stack gas effluents of hazardous waste incinerators using the Volatile Organic Sampling Train (VOST) methodology (1) with analysis by GC/MS (Method 8260). For a comprehensive description of the VOST sampling methodology see Method 0030. The following compounds may be determined by this method:

Compound	CAS No.[a]
Acetone	67-64-1
Acrylonitrile	107-13-1
Benzene	71-43-2
Bromodichloromethane	75-27-4
Bromoform[b]	75-25-2
Bromomethane[c]	74-83-9
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chlorodibromomethane	124-48-1
Chloroethane[c]	75-00-3
Chloroform	67-66-3
Chloromethane[c]	74-87-3
Dibromomethane	74-95-3
1,1-Dichloroethane	75-35-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene[b]	100-41-4
Iodomethane	74-88-4
Methylene chloride	75-09-2
Styrene[b]	100-42-5
1,1,2,2-Tetrachloroethane[b]	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5

(continued)

Compound	CAS No.[a]
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane[b]	96-18-4
Vinyl chloride[c]	75-01-4
Xylenes[b]	

[a] Chemical Abstract Service Registry Number.

[b] Boiling point of this compound is above 120°C. Method 0030 is not appropriate for quantitative sampling of this analyte.

[c] Boiling point of this compound is below 30°C. Special precautions must be taken when sampling for this analyte by Method 0030. Refer to Sec. 1.3 for discussion.

1.2 This method is most successfully applied to the analysis of non-polar organic compounds with boiling points between 30°C and 100°C. Data are applied to the calculation of destruction and removal efficiency (DRE), with limitations discussed below.

1.3 This method may be applied to analysis of many compounds which boil above 100°C, but Method 0030 is always inappropriate for collection of compounds with boiling points above 120°C. All target analytes with boiling points greater than 120°C are so noted in the target analyte list presented in Sec. 1.1. Use of Method 0030 for collection of compounds boiling between 100°C and 120°C is often possible, and must be decided based on case by case inspection of information such as sampling method collection efficiency, tube desorption efficiency, and analytical method precision and bias. An organic compound with a boiling point below 30°C may break through the sorbent under the conditions used for sample collection. Quantitative values obtained for compounds with boiling points below 30°C must be qualified, since the value obtained represents a minimum value for the compound if breakthrough has occurred. In certain cases, additional QC measures may have been taken during sampling very low boilers with Method 0030. This information should be considered during the data interpretation stage.

1.4 When Method 5041 is used for survey analyses, values for compounds boiling above 120°C may be reported and qualified since the quantity obtained represents a minimum value for the compound. These minimum values should not be used for trial burn DRE calculations or to prove insignificant risk.

1.5 The VOST analytical methodology can be used to quantitate volatile organic compounds that are insoluble or slightly soluble in water. When volatile, water soluble compounds are included in the VOST organic compound analyte list, quantitation limits can be expected to be approximately ten times higher than quantitation limits for water insoluble compounds (if the compounds can be recovered at all) because the purging efficiency from water (and possibly from Tenax-GC®) is poor.

1.6 Overall sensitivity of the method is dependent upon the level of interferences encountered in the sample and the presence of detectable concentrations of volatile POHCs in blanks. The target detection limit of this method is 0.1 $\mu g/m^3$ (ng/L) of flue gas, to permit calculation of a DRE equal to or greater than 99.99% for volatile POHCs which may be present in the waste stream at 100 ppm. The upper end of the range of applicability of this method is limited by the dynamic range of the

analytical instrumentation, the overall loading of organic compounds on the exposed tubes, and breakthrough of the volatile POHCs on the sorbent traps used to collect the sample. Method 8260 presents method detection limits for a range of volatile compounds analyzed by this method interfaced to a GC/MS with wide bore capillary methodology.

1.7 This method is restricted to use by, or under the supervision of, analysts experienced in the use of sorbent media, purge-and-trap systems, and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The sorbent tubes are thermally desorbed by heating and purging with organic-free helium. The gaseous effluent from the tubes is bubbled through pre-purged organic-free reagent water and trapped on an analytical sorbent trap in a purge-and-trap unit (Figure 2).

2.2 After desorption, the analytical sorbent trap is heated rapidly and the gas flow from the analytical trap is directed to the head of a wide-bore column under subambient conditions.

2.3 The volatile organic compounds desorbed from the analytical trap are determined by Method 8260 (Figure 3).

3.0 INTERFERENCES

3.1 Sorbent tubes which are to be analyzed for volatile organic compounds can be contaminated by diffusion of volatile organic compounds (particularly Freon® refrigerants and common organic solvents) through the external container [even through a polytetrafluoroethylene (PTFE)-lined screw cap on a glass container] and the Swagelok® sorbent tube caps during shipment and storage. The sorbent tubes can also be contaminated if organic solvents are present in the analytical laboratory. The use of blanks is essential to assess the extent of any contamination. Field blanks need to be prepared and taken to the field. The end caps of the tubes are removed for the period of time required to exchange two pairs of traps on the VOST sampling apparatus. The tubes are recapped and shipped and handled exactly as the actual field samples are shipped and handled. At least one pair of field blanks is included with each six pairs of sample cartridges collected.

3.2 At least one pair of blank cartridges (one Tenax-GC®, one Tenax-GC®/charcoal) must be included with shipment of cartridges to a hazardous waste incinerator site as trip blanks. These trip blanks are treated like field blanks except that the end caps are not removed during storage at the site. This pair of traps are analyzed to monitor potential contamination which may occur during storage and shipment.

3.3 Analytical system blanks are needed to demonstrate that contamination of the purge-and-trap unit and the gas chromatograph/mass spectrometer has not occurred or that, in the event of analysis of sorbent tubes with very high concentrations of organic compounds, no compound carryover is occurring. Tenax® from the same preparation batch as the Tenax® used for field sampling should be used in the preparation of the method (laboratory) blanks. A sufficient number of cleaned Tenax® tubes from the same batch as the field samples should be reserved in the laboratory for use as blanks.

3.4 Cross contamination can occur whenever low-concentration samples are analyzed after high-concentration samples, or when several high-concentration samples are analyzed sequentially.

When an unusually concentrated sample is analyzed, this analysis should be followed by a method blank to establish that the analytical system is free of contamination. If analysis of a blank demonstrates that the system is contaminated, an additional bake cycle should be used. If the analytical system is still contaminated after additional baking, routine system maintenance should be performed: the analytical trap should be changed and conditioned, routine column maintenance should be performed (or replacement of the column and conditioning of the new column, if necessary), and bakeout of the ion source (or cleaning of the ion source and rods, if required). After system maintenance has been performed, analysis of a blank is needed to demonstrate that the cleanliness of the system is acceptable.

3.5 Impurities in the purge gas and from organic compounds out-gassing in tubing account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing two sets of clean, blank sorbent tubes with organic-free reagent purge water as system blanks. The analytical system is acceptably clean when these two sets of blank tubes show values for the analytes which are within one standard deviation of the normal system blank. Use of plastic coatings, non-PTFE thread sealants, or flow controllers with rubber components should be avoided.

3.6 VOST tubes are handled in the laboratory to spike standards and to position the tubes within the desorption apparatus. When sorbent media are handled in the laboratory atmosphere, contamination is possible if there are organic solvents in use anywhere in the laboratory. It is therefore necessary to make daily use of system blanks to monitor the cleanliness of the sorbents and the absence of contamination from the analytical system. A single set of system blank tubes shall be exposed to normal laboratory handling procedures and analyzed as a sample. This sample should be within one standard deviation of normal VOST tube blanks to demonstrate lack of contamination of the sorbent media.

3.7 If the emission source has a high concentration of non-target organic compounds (for example, hydrocarbons at concentrations of hundreds of ppm), the presence of these non-target compounds will interfere with the performance of the VOST analytical methodology. If one or more of the compounds of interest saturates the chromatographic and mass spectrometric instrumentation, no quantitative calculations can be made and the tubes which have been sampled under the same conditions will yield no valid data for any of the saturated compounds. In the presence of a very high organic loading, even if the compounds of interest are not saturated, the instrumentation is so saturated that the linear range has been surpassed. When instrument saturation occurs, it is possible that compounds of interest cannot even be identified correctly because a saturated mass spectrometer may mis-assign masses. Even if compounds of interest can be identified, accurate quantitative calculations are impossible at detector saturation. No determination can be made at detector saturation, even if the target compound itself is not saturated. At detector saturation, a negative bias will be encountered in analytical measurements and no accurate calculation can be made for the Destruction and Removal Efficiency if analytical values may be biased negatively.

3.8 The recoveries of the surrogate compounds, which are spiked on the VOST tubes immediately before analysis, should be monitored carefully as an overall indicator of the performance of the methodology. Since the matrix of stack emissions is so variable, only a general guideline for recovery of 50-150% can be used for surrogates. The analyst cannot use the surrogate recoveries as a guide for correction of compound recoveries. The surrogates are valuable only as a general indicator of correct operation of the methodology. If surrogates are not observed or if recovery of one or more of the surrogates is outside the 50-150% range, the VOST methodology is not operating correctly. The cause of the failure in the methodology is not obvious. The matrix of stack emissions contains large amounts of water, may be highly acidic, and may contain large amounts of target and

non-target organic compounds. Chemical and surface interactions may be occurring on the tubes. If recoveries of surrogate compounds are extremely low or surrogate compounds cannot even be identified in the analytical process, then failure to observe an analyte may or may not imply that the compound of interest has been removed from the emissions with a high degree of efficiency (that is, the DRE for that analyte is high).

4.0 APPARATUS AND MATERIALS

4.1 Tube desorption apparatus: Acceptable performance of the methodology requires:

1) temperature regulation to ensure that tube temperature during desorption is regulated to 180°C ± 10°;

2) good contact between tubes and the heating apparatus to ensure that the sorbent bed is thoroughly and uniformly heated to facilitate desorption of organic compounds; and

3) gas-tight connections to the ends of the tubes to ensure flow of desorption gas through the tubes without leakage during the heating/desorption process. A simple clamshell heater which will hold tubes which are 3/4" in outer diameter will perform acceptably as a desorption apparatus.

4.2 Purge-and-trap device: The purge-and-trap device is described in Method 5030, Sec. 4.0.

4.2.1 The cartridge thermal desorption apparatus is connected to the sample purge vessel by 1/16" PTFE (e.g., Teflon®) tubing (unheated transfer line). The tubing which connects the desorption chamber to the sample purge vessel should be as short as is practical.

4.2.2 The sample purge vessel is required to hold 5 mL of organic-free reagent water, through which the gaseous effluent from the VOST tubes is routed.

4.3 The gas chromatograph/mass spectrometer/data system and recommended GC columns are described in Method 8260, Sec. 4.0.

4.4 Wrenches: 9/16", 1/2", 7/16", and 5/16".

4.5 PTFE (e.g., Teflon®) tubing: 1/16" diameter.

4.6 Syringes: 25 µL syringes (2), 10 µL syringes (2).

4.7 Fittings: 1/4" nuts, 1/8" nuts, 1/16" nuts, 1/4" to 1/8" union, 1/4" to 1/4" union, 1/4" to 1/16" union.

4.8 Adjustable stand to raise the level of the desorption unit, if necessary.

4.9 Volumetric flasks: 5 mL, class A with ground glass stopper.

4.10 Injector port or equivalent, heated to 180°C for loading standards onto VOST tubes prior to analysis.

4.11 Vials: 2 mL, with PTFE-lined screw caps or crimp tops.

4.12 Syringe: 5 mL, gas-tight with shutoff valve.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

NOTE: It is advisable to maintain the stock of organic-free reagent water generated for use in the purge-and-trap apparatus with a continuous stream of inert gas bubbled through the water. Continuous bubbling of the inert gas maintains a positive pressure of inert gas above the water as a safeguard against contamination.

5.3 Methanol, CH_3OH. Pesticide quality or equivalent. To avoid contamination with other laboratory solvents, it is advisable to maintain a separate stock of methanol for the preparation of standards for VOST analysis and to regulate the use of this methanol very carefully.

5.4 Surrogate standards: The recommended surrogates are listed in Method 8260, Sec. 5.0. A stock surrogate compound solution in high purity methanol should be prepared as described in Sec. 5.0, Method 8260, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 µg/10 mL in high purity methanol. Each pair of VOST tubes (or each individual VOST tube, if the tubes are analyzed separately) must be spiked with 10 µL of the surrogate spiking solution prior to GC/MS analysis.

5.5 Internal standards: The recommended internal standards for GC/MS analysis are listed in Method 8260, Sec. 5.0. Prepare internal standard stock and secondary dilution standards in high purity methanol using the procedures described in Sec. 5.0 of Method 8260. The secondary dilution standard should be prepared at a concentration of 25 mg/L of each of the internal standard compounds. Addition of 10 µL of this internal standard solution to each pair of VOST tubes (or to each VOST tube, if the tubes are analyzed individually) is the equivalent of 250 ng total.

5.6 Great care must be taken to maintain the integrity of all standard solutions. All standards of volatile compounds in methanol should be stored at -10°C to -20°C in amber bottles with PTFE-lined screw caps or crimp tops. In addition, careful attention must be paid to the use of syringes designated for a specific purpose or for use with only a single standard solution since cross contamination of volatile organic standards can occur very readily.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Method 0030 or Method 0031 for VOST Sampling Methodology.

6.2 VOST samples are collected on paired cartridges. The first of the pair of sorbent cartridges is packed with approximately 1.6 g of Tenax-GC® resin. The second cartridge of the pair is packed with Tenax-GC® and petroleum based charcoal (3:1 by volume; approximately 1 g of each). In sampling, the emissions gas stream passes through the Tenax-GC® layer first and then through the charcoal layer. The Tenax-GC® is cleaned and reused; charcoal is not reused when tubes are prepared. Sorbent is cleaned and the tubes are packed. The tubes are desorbed and subjected to a blank check prior to being sent to the field. When the tubes are used for sampling (see Figure 5 for a schematic diagram of the VOST), cooling water is circulated to the condensers and the temperature of the cooling water is maintained near 0°C. The end caps of the sorbent cartridges are placed in a clean, screw capped glass container during sample collection.

6.3 After the apparatus is leak checked, sample collection is accomplished by opening the valve to the first condenser, turning on the pump, and sampling at a rate of 1 L/min for 20 minutes. The volume of sample for any pair of traps should not exceed 20 liters. An alternative set of conditions for sample collection requires sampling at a reduced flow rate, where the overall volume of sample collected is 5 liters at a rate of 0.25 L/min for 20 minutes. The 20 minute period is necessary for collecting an integrated sample.

6.4 Following collection of 20 Liters of sample, the train is leak checked a second time at the highest pressure drop encountered during the run to minimize the chance of vacuum desorption of organics from the Tenax®.

6.5 The train is returned to atmospheric pressure and the two sorbent cartridges are removed. The end caps are replaced and the cartridges are placed in a suitable environment for storage and transport until analysis. The sample is considered invalid if the leak test does not meet specifications.

6.6 A new pair of cartridges is placed in the VOST, the VOST is leak checked, and the sample collection process is repeated until all pairs of traps have been exposed.

6.7 All sample cartridges are kept in coolers on cold packs after exposure and during shipment. Upon receipt at the laboratory, the cartridges are stored in a refrigerator at 4°C until analysis. The maximum storage time between sampling and analysis is 14 days.

7.0 PROCEDURE

7.1 Recommended operating conditions for cartridge desorber and purge-and-trap unit, are:

<u>Cartridge Desorption Oven</u>	
Desorb Temperature	180°C
Desorb Time	11 minutes
Desorption Gas Flow	40 mL/min
Desorption/Carrier Gas	Helium, Grade 5.0
<u>Purge-and-Trap Concentrator</u>	
Analytical Trap Desorption Flow	2.5 mL/min helium
Purge Temperature	Ambient
Purge Time	11 minutes
Analytical Trap Desorb Temp.	180°C
Analytical Trap Desorb Time	5 minutes

Gas Chromatograph

Column	30 m x 0.53 mm ID, coated with DB-624 (J&W Scientific), 3 µm film thickness, or equivalent.
Carrier Gas Flow	15 mL/min
Makeup Gas Flow	15 mL/min
Injector Temperature	200°C
Transfer Oven Temperature	240°C
Initial Temperature	5°C
Initial Hold Time	2 minutes
Program Rate	6°C/min
Final Temperature	240°C
Final Hold Time	1 minute or until elution ceases

Mass Spectrometer

Manifold Temperature	105°C
Scan Rate	1 sec/cycle
Mass Range	35-260 amu
Electron Energy	70 eV (nominal)
Source Temperature	According to manufacturer's specifications

7.2 Each GC/MS system must be hardware tuned to meet the BFB criteria in Method 8260.

7.3 Assemble and operate a purge-and-trap device as per Method 5030.

7.4 Connect the purge-and-trap device to a gas chromatograph.

7.5 Assemble a VOST tube desorption apparatus which meets the requirements of Sec. 4.1.

7.6 Connect the VOST tube desorption apparatus to the purge-and-trap unit.

7.7 Spiking standards onto VOST tubes: For this procedure, the system will be calibrated using the internal standard procedure. Internal standards, surrogates, and calibration standards in methanolic solution will be spiked onto cleaned VOST tubes for proper calibration of the system. These standards are spiked onto VOST tubes using the flash evaporation technique. To perform flash evaporation, the injector of a gas chromatograph or an equivalent piece of equipment is required.

7.7.1 Prepare a syringe with the appropriate volume of methanolic standard solution (either surrogates, internal standards, or calibration compounds).

7.7.2 With the injector port heated to 180°C, and with an inert gas flow of 10 mL/min through the injector port, connect the paired VOST tubes (connected as in Figure 1, with gas flow in the same direction as the sampling gas flow) to the injector port; tighten with a wrench so that there is no leakage of gas. If separate tubes are being analyzed, an individual Tenax® or Tenax®/charcoal tube is connected to the injector.

7.7.3 After directing the gas flow through the VOST tubes, slowly inject the first standard solution over a period of 25 seconds. Wait for 5 seconds before withdrawing the syringe from the injector port.

7.7.4 Inject a second standard (if required) over a period of 25 seconds and wait for 5 seconds before withdrawing the syringe from the injector port.

7.7.5 Repeat the sequence above, as required, until all of the necessary compounds are spiked onto the VOST tubes.

7.7.6 Wait for 30 seconds, with gas flow, after the last spike before disconnecting the tubes. The total time the tubes are connected to the injector port with gas flow should not exceed 2.5 minutes. Total gas flow through the tubes during the spiking process should not exceed 25 mL to prevent break-through of adsorbed compounds during the spiking process. To allow more time for connecting and disconnecting tubes, an on/off valve may be installed in the gas line to the injector port so that gas is not flowing through the tubes during the connection/disconnection process.

7.8 Prepare the purge-and-trap unit with 5 mL of organic-free reagent water in the purge vessel.

7.9 Connect the paired VOST tubes to the gas lines in the tube desorption unit. The tubes must be connected so that the gas flow during desorption will be opposite to the flow of gas during sampling: i.e., the tube desorption gas passes through the charcoal portion of the tube first. An on/off valve may be installed in the gas line leading to the tube desorption unit in order to prevent flow of gas through the tubes during the connection process.

7.10 Initiate tube desorption/purge and heating of the VOST tubes in the desorption apparatus.

7.11 Cool the oven of the gas chromatograph to subambient temperature with liquid nitrogen.

7.12 Prepare the GC/MS system for data acquisition as per Method 8260.

7.13 At the conclusion of the tube/water purge time, attach the analytical trap to the gas chromatograph, adjust the purge-and-trap device to the desorb mode, and initiate the gas chromatographic program and the GC/MS data acquisition. Perform the remainder of the purge and trap process as described in Method 5030, Sec. 7.

7.14 Initial calibration for the analysis of VOST tubes: It is essential that calibration be performed in the mode in which analysis will be performed. If tubes are being analyzed as pairs, calibration standards should be prepared on paired tubes. If tubes are being analyzed individually, a calibration should be performed on individual Tenax® only tubes and Tenax®/charcoal tubes.

7.14.1 Prepare the calibration standards by spiking VOST tubes using the procedure described in Sec. 7.7. Spike each pair of VOST tubes (or each of the individual tubes) immediately before analysis. Perform the calibration analyses in order from low concentration to high to minimize the compound carryover. Add 5.0 mL of organic-free reagent water to the purging vessel. Initiate tube desorb/purge according to the procedure.

7.14.2 Continue the initial calibration process as described in Method 8260, Sec. 7.0. The same criteria for SPCC, CCC and linearity must be met.

7.15 GC/MS Calibration Verification

7.15.1 Prior to the analysis of samples, purge 5-50 ng of the 4-bromofluorobenzene standard. The resultant mass spectrum for BFB must meet all of the criteria given in Method 8260 before sample analysis begins. These criteria must be demonstrated every twelve hours of operation.

7.15.2 Perform calibration verification as per Method 8260, Sec. 7.0. The same criteria for SPCC, linearity and internal standard response check must be met. See the next section for special guidance on the CCCs.

7.15.3 If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. Benzene, toluene, and styrene will have problems with response factors if Tenax® decomposition occurs (either as a result of sampling exposure or temperature degradation), since these compounds are decomposition products of Tenax®. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion of percent difference less than 25% is not met for any one CCC, corrective action MUST be taken. If a source of the problem cannot be determined after corrective action is taken, a new five-point calibration curve MUST be generated. The criteria for the CCCs MUST be met before quantitative analysis can begin.

7.15.4 Internal standard responses and retention times in the calibration verification standard must be evaluated immediately after or during data acquisition. A factor which may influence the retention times of the internal standards on sample tubes is the level of overall organic compound loading on the VOST tubes. If the VOST tubes are very highly loaded with either a single compound or with multiple compounds, retention times for standards and compounds of interest will be affected. If the area for the primary ion of any of the internal standards changes by a factor of two (-50% to +100%) from the last calibration verification standard, the gas chromatograph and mass spectrometer should be inspected for malfunctions and corrections must be made, as appropriate. If the level of organic loading of samples is high, areas for the primary ions of both compounds of interest and standards will be adversely affected. Calibration verification standards should not be subject to variation, since the concentrations of organic compounds on these samples are set to be within the linear range of the instrumentation. If instrument malfunction has occurred, analyses of samples performed under conditions of malfunction may be invalidated.

7.16 GC/MS Analysis of Samples

7.16.1 Set up the cartridge desorption unit, purge-and-trap unit (Method 5030), and GC/MS (Method 8260) as described above or as described in the indicated methods.

7.16.2 BFB tuning criteria and GC/MS calibration verification criteria in Method 8260 must be met before analyzing samples. (See Sec. 7.15)

7.16.3 Adjust the helium purge gas flow rate (through the cartridges and purge vessel) to approximately 40 mL/min. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. A flow rate which is too high reduces the recovery of chloromethane, and an insufficient gas flow rate reduces the recovery of bromoform.

7.16.4 The first analysis performed after the tuning check and the calibration or calibration verification should be a method blank. The method blank consists of clean VOST tubes (both Tenax® and Tenax®/charcoal) which are spiked with surrogate compounds and internal standards according to the procedure described in Sec. 7.7. The tubes which are used for the method blanks should be from the same batch of sorbent as the sorbent used for the field samples. After the tubes are cleaned and prepared for shipment to the field, sufficient pairs of tubes should be retained from the same batch in the laboratory to provide method blanks during the analysis.

7.16.5 Use organic-free reagent water as described in Chapter One for the purge vessel.

7.16.6 If the analysis of a pair of VOST tubes has a concentration of analytes that exceeds the initial calibration range, no reanalysis of desorbed VOST tubes is possible. An additional calibration point can be added to bracket the higher concentration encountered in the samples so that the calibration database encompasses six or more points. Alternatively, the data may be flagged in the report as "extrapolated beyond the upper range of the calibration."

7.16.7 The use of the secondary ions shown in Method 8260 is permissible only in the case of interference with the primary quantitation ion. Use of secondary ions to calculate compound concentration in the case of saturation of the primary ion is not an acceptable procedure, since a negative bias of an unpredictable magnitude is introduced into the quantitative data when saturation of the mass spectrum of a compound is encountered.

7.16.8 If high organic loadings, either of a single compound or of multiple compounds, are encountered, it is vital that a method blank be analyzed prior to the analysis of another sample to demonstrate that no compound carryover is occurring. If concentrations of organic compounds are sufficiently high that carryover problems are profound, extensive bakeout of the purge-and-trap unit is necessary. More extensive guidance on corrective maintenance of the purge and trap and GC/MS system are found in Sec. 7.0 of their respective methods (Method 5030 and Method 8260).

7.17 Qualitative analysis: Follow the procedure on qualitative analysis found in Sec. 7.0 of Method 8260.

7.18 Quantitative analysis: See Method 8260 for overall information on alternative approaches to quantitation.

7.18.1 Calculate the amount in ng of each identified analyte from the VOST tubes following the guidance on calculations presented in Sec. 7.0 of Method 8260.

7.18.2 The choice of methods for evaluating data collected using the VOST methodology for incinerator trial burns is a regulatory decision. Contact the local regulatory agencies to which VOST data are submitted for information on data reporting preferences.

7.18.3 The total amount of the POHCs of interest collected on a pair of traps should be summed.

7.18.4 The occurrence of high concentrations of analytes on method blank cartridges indicates possible residual contamination of sorbent cartridges prior to shipment and use at the sampling site. Data with high associated blank values must be qualified with respect to validity, and all blank data should be reported separately. No blank corrections should be made in this case. Whether or not data of this type can be applied to the determination of destruction and removal efficiency is a regulatory decision. Continued observation of high concentrations of analytes on blank sorbent cartridges indicates that procedures for cleanup and quality control for the sampling tubes are inadequate. Corrective action must be applied to tube preparation and monitoring procedures to maintain method blank concentrations below detection limits for analytes.

7.18.5 Where applicable, an estimate of concentration for noncalibrated components in the sample may be made. Follow the guidance in Method 8260, Sec. 7.0 that covers this issue.

7.18.6 If any internal standard recoveries fall outside the control limits established in Section 8.4, data for all analytes determined for that cartridge(s) must be qualified with the observation. Report results without correction for surrogate compound recovery data. When duplicates are analyzed, report the data obtained with the sample results.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Sec. 8.0 of Methods 5000 and 8000 for specific quality control procedures. Each laboratory using SW-846 methods should maintain a formal quality assurance program.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank (laboratory blank sorbent tubes, reagent water purge) that interferences from the analytical system, glassware, sorbent tube preparation, and reagents are under control. Each time a new batch of sorbent tubes is analyzed, a method blank should be processed as a safeguard against chronic laboratory contamination. Blank tubes which have been carried through all the stages of sorbent preparation and handling should be used in the analysis.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory should also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.3.1 A reference sample concentrate is needed containing each analyte at a concentration of 10 mg/L in high purity methanol. The reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If the reference sample concentrate is prepared by the laboratory, it must be prepared using stock standards prepared independently from the stock standards used for calibration.

8.3.2 Spike four pairs of cleaned, prepared VOST tubes with 10 µL of the QC check sample concentrate and analyze these spiked VOST tubes according to the method beginning in Sec. 7.0.

8.3.3 Calculate the average recovery (X) in ng and the standard deviation of the recovery (s) in ng for each analyte using the results of the four analyses.

8.3.4 The average recovery and standard deviation must fall within the expected range for determination of volatile organic compounds using the VOST analytical methodology. The expected range for recovery of volatile organic compounds using this method is 50-150%. Standard deviation will be compound dependent, but should, in general, range from 15 to 30 ng. More detailed method performance criteria must be generated from historical records in the laboratory or from interlaboratory studies coordinated by the Environmental Protection Agency. Since the additional steps of sorbent tube spiking and desorption are superimposed upon the methodology of Method 8260, direct transposition of Method 8260 criteria is questionable. If the recovery and standard deviation for all analytes meet the acceptance

criteria, the system performance is acceptable and the analysis of field samples may begin. If any individual standard deviation exceeds the precision limit or any individual recovery falls outside the range for accuracy, then the system performance is unacceptable for that analyte. See also further information on this subject found in Method 8000, Sec. 8.0.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. This includes the method blank (Sec. 8.2), a laboratory control sample (LCS) and the addition of surrogates to each sample and QC sample.

8.4.1 The LCS is prepared by spiking reference sample concentrate (noted in Sec. 8.3) onto a clean VOST tube.

8.4.2 If surrogate recovery is not within the limits established by the laboratory, the following procedures are necessary: (1) Verify that there are no errors in calculations, preparation of surrogate spiking solutions, and preparation of internal standard spiking solutions. Also, verify that instrument performance criteria have been met. (2) Recalculate the data and/or analyze a replicate sample, if replicates are available. (3) If all instrument performance criteria are met and recovery of surrogates from spiked blank VOST tubes (analysis of a method blank) is acceptable, the problem is due to the matrix. Emissions samples may be highly acidic and may be highly loaded with target and non target organic compounds. Both of these conditions will affect the ability to recover surrogate compounds which are spiked on the field samples. The surrogate compound recovery is thus a valuable indicator of the interactions of sampled compounds with the matrix. If surrogates spiked immediately before analysis cannot be observed with acceptable recovery, the implications for target organic analytes which have been sampled in the field must be assessed very carefully. If chemical or other interactions are occurring on the exposed tubes, the failure to observe an analyte may not necessarily imply that the DRE for that analyte is high.

9.0 METHOD PERFORMANCE

9.1 Method detection limit (MDL) is defined in Chapter One. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix.

9.2 The MDL concentrations for VOST analytes can be found in Sec. 9.0 of Method 8260.

10.0 REFERENCES

1. Protocol for Collection and Analysis of Volatile POHCs Using VOST. EPA/600/8-84-007, March, 1984.

2. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.

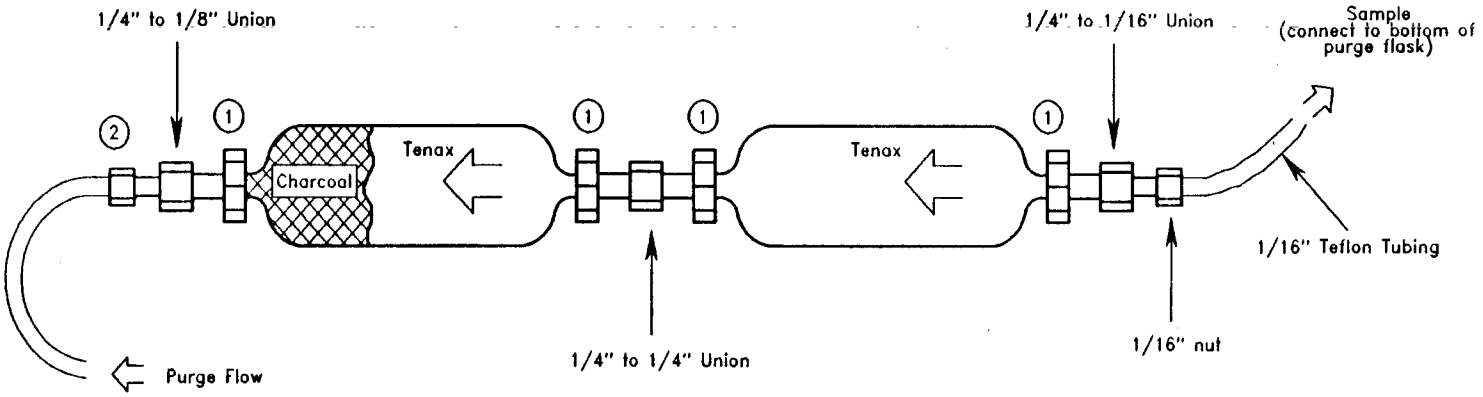
3. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act, Method 624," October 26, 1984.

4. Bellar, T. A., and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), 739-744, 1974.

5. Bellar, T. A., and J.J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.

FIGURE 1

CARTRIDGE DESORPTION FLOW



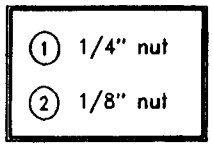


FIGURE 2

CARTRIDGE DESORPTION UNIT WITH PURGE AND TRAP UNIT

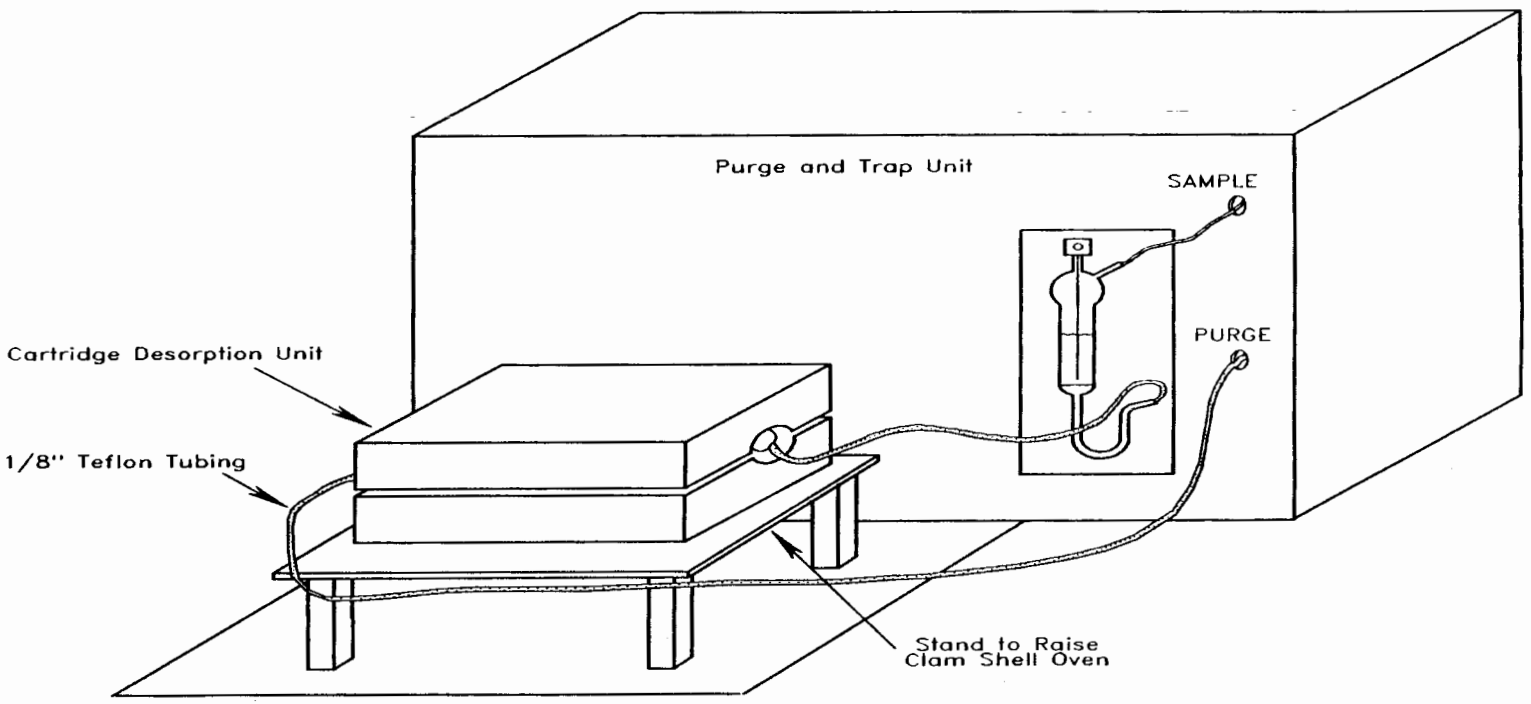


FIGURE 3

SCHEMATIC DIAGRAM OF ANALYTICAL SYSTEM

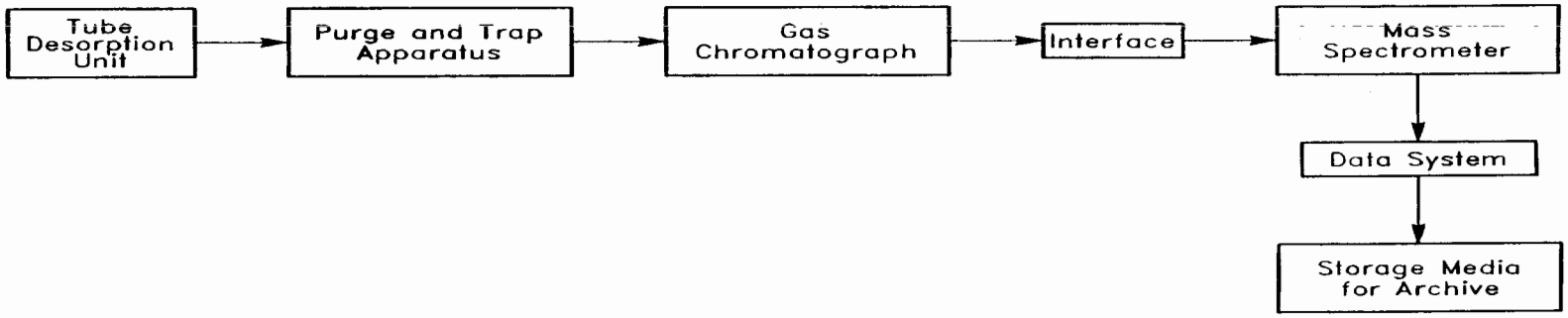


FIGURE 4

SAMPLE PURGE VESSEL

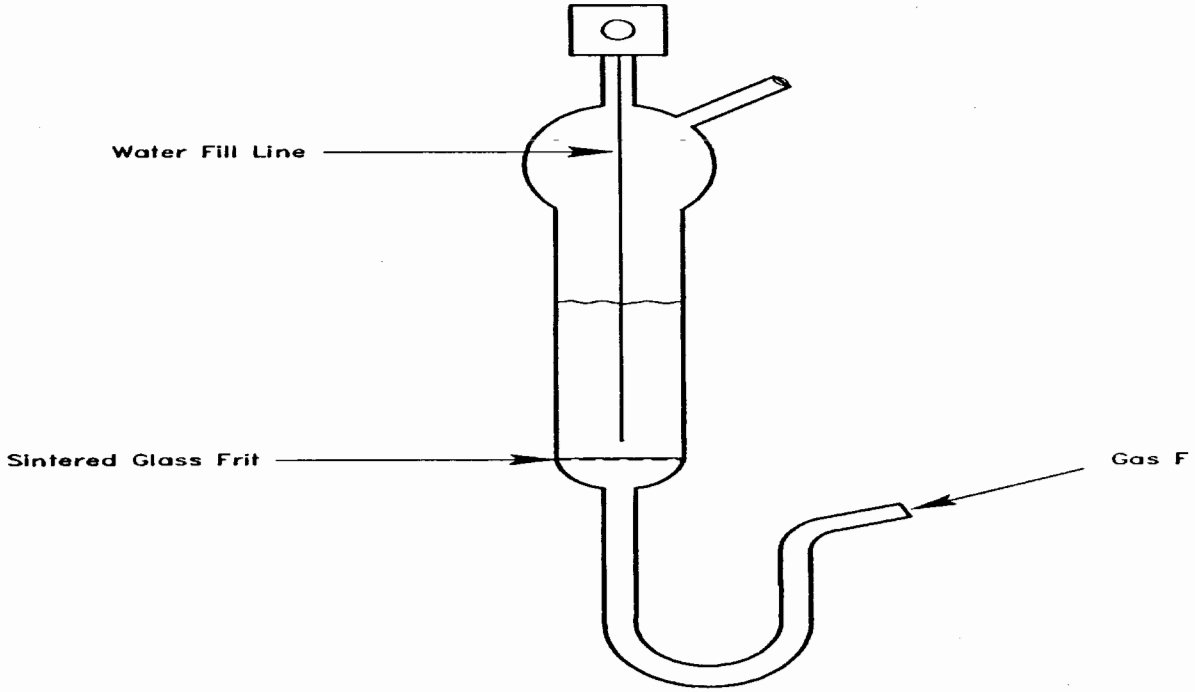
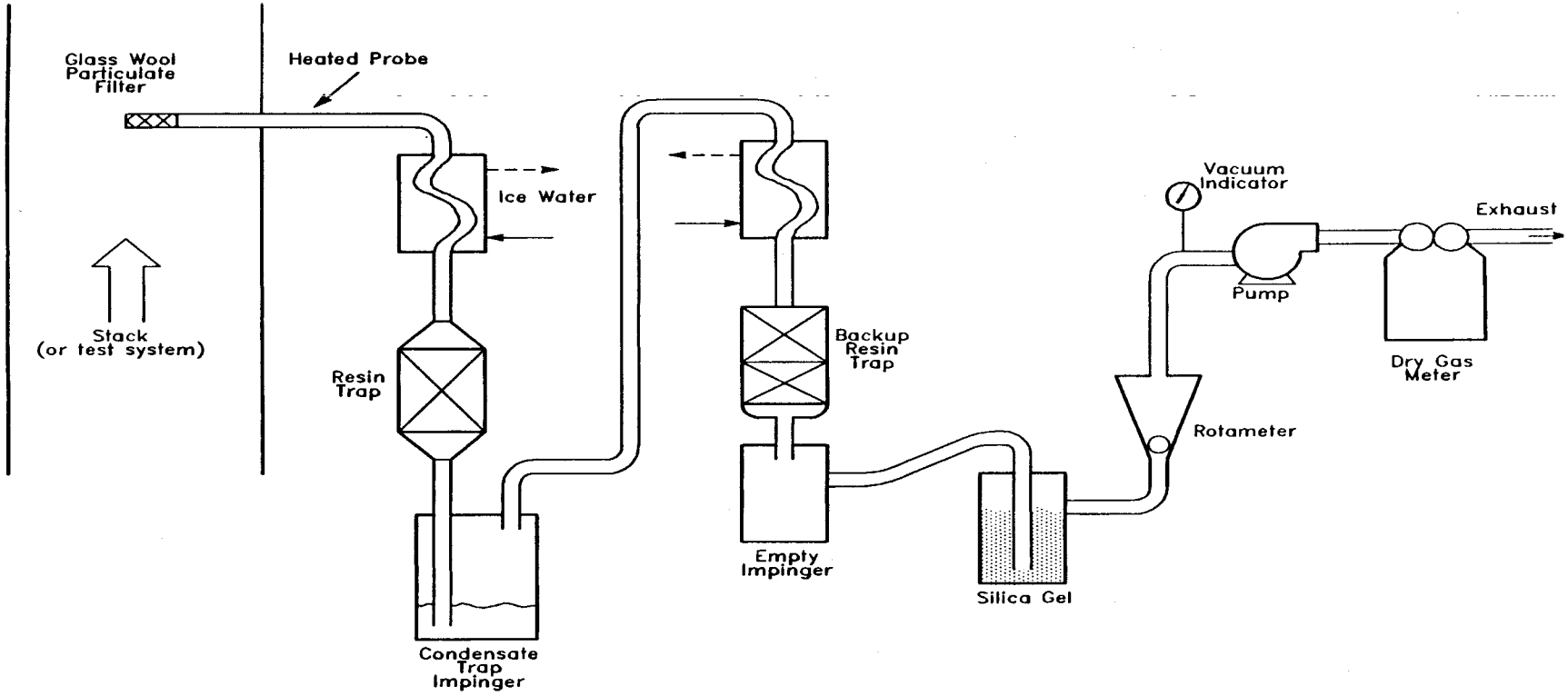
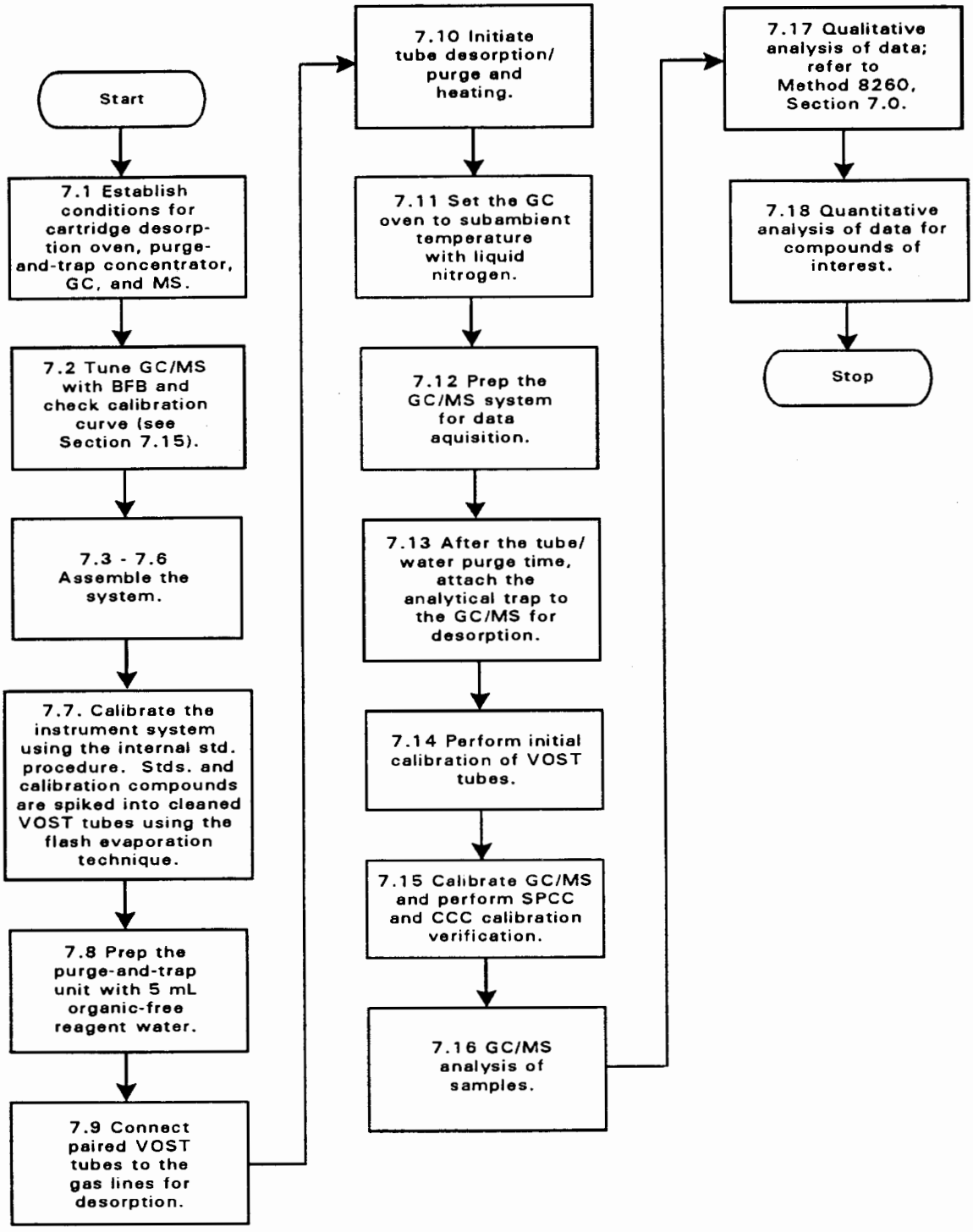


FIGURE 5

SCHEMATIC OF VOLATILE ORGANIC SAMPLING TRAIN (VOST)



ANALYSIS FOR DESORPTION OF SORBENT CARTRIDGES FROM
VOLATILE ORGANIC SAMPLING TRAIN (VOST)



METHOD 5050

BOMB PREPARATION METHOD FOR SOLID WASTE

1.0 SCOPE AND APPLICATION

1.1 This method describes the sample preparation steps necessary to determine total chlorine in solid waste and virgin and used oils, fuels and related materials, including: crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by bomb oxidation and titration or ion chromatography. Depending on the analytical finish chosen, other halogens (bromine and fluorine) and other elements (sulfur and nitrogen) may also be determined.

1.2 The applicable range of this method varies depending on the analytical finish chosen. In general, levels as low as 500 µg/g chlorine in the original oil sample can be determined. The upper range can be extended to percentage levels by dilution of the combustate.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific safety statements are given in Section 3.0.

2.0 SUMMARY OF METHOD

2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure. The liberated halogen compounds are absorbed in a sodium carbonate/sodium bicarbonate solution. Approximately 30 to 40 minutes are required to prepare a sample by this method. Samples with a high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion. Complete combustion is still not guaranteed for such samples.

2.2 The bomb combustate solution can then be analyzed for the following elements as their anion species by one or more of the following methods:

Method	Title
9252	Chloride (Titrimetric, Mercuric Nitrate)
9253	Chloride (Titrimetric, Silver Nitrate)
9056	Inorganic Anions by Ion Chromatography (Chloride, Sulfate, Nitrate, Phosphate, Fluoride, Bromide)

NOTE: Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the bomb, or a blowout, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 1/2 in. (12.7 mm) thick, or equivalent protection be provided against unforeseeable contingencies.

3.0 INTERFERENCES

3.1 Samples with very high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion.

3.2 To determine total nitrogen in samples, the bombs must first be purged of ambient air. Otherwise, nitrogen results will be biased high.

4.0 APPARATUS AND MATERIALS

4.1 Bomb, having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action and shall not undergo any reaction that will affect the chlorine content of the sample in the bomb.

4.2 Sample cup, platinum or stainless steel, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g.

4.3 Firing wire, platinum or stainless steel, approximately No. 26 B & S gage.

4.4 Ignition circuit, capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

NOTE: The switch in the ignition circuit shall be of the type that remains open, except when held in closed position by the operator.

4.5 Nylon sewing thread, or Cotton Wicking, white.

4.6 Funnel, to fit a 100-mL volumetric flask.

4.7 Class A volumetric flasks, 100-mL, one per sample.

4.8 Syringe, 5- or 10-mL disposable plastic or glass.

4.9 Apparatus for specific analysis methods are given in the methods.

4.10 Analytical balance: capable of weighing to 0.0001 g.

5.0 REAGENTS

5.1 Purity of reagents. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Oxygen. Free of combustible material and halogen compounds, available at a pressure of 40 atm.

WARNING: Oxygen vigorously accelerates combustion (see Appendix A1.1)

5.4 Sodium bicarbonate/sodium carbonate solution. Dissolve 2.5200 g $NaHCO_3$ and 2.5440 g Na_2CO_3 in reagent water and dilute to 1 L.

5.5 White oil. Refined.

5.6 Reagents and materials for specific analysis methods are given in the methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Ensure that the portion of the sample used for the test is representative of the sample.

6.3 To minimize losses of volatile halogenated solvents that may be present in the sample, keep the field and laboratory samples as free of headspace as possible.

6.4 Because used oils may contain toxic and/or carcinogenic substances appropriate field and laboratory safety procedures should be followed.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Preparation of bomb and sample. Cut a piece of firing wire approximately 100 mm in length and attach the free ends to the terminals. Arrange the wire so that it will be just above and not touching the sample cup. Loop a cotton thread around the wire so that the ends will extend into the sampling cup. Pipet 10 mL of the $NaHCO_3/Na_2CO_3$ solution into the bomb, wetting the sides. Take an aliquot of the oil sample of approximately 0.5 g using a 5- or 10-mL disposable plastic syringe, and place in

the sample cup. The actual sample weight is determined by the difference between the weight of the empty and filled syringe. Do not use more than 1 g of sample.

NOTE: After repeated use of the bomb for chlorine determination, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 rpm and polish the inside surface with Grit No. 2/0 or equivalent paper[1] coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide[2] and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the bomb, it should be washed with soap and water to remove oil or paste left from the polishing operation. Bombs with porous or pitted surfaces should never be used because of the tendency to retain chlorine from sample to sample.

NOTE: If the sample is not readily combustible, other nonvolatile, chlorine-free combustible diluents such as white oil may be employed. However, the combined weight of sample and nonvolatile diluent shall not exceed 1 g. Some solid additives are relatively insoluble but may be satisfactorily burned when covered with a layer of white oil.

NOTE: The practice of alternately running samples high and low in chlorine content should be avoided whenever possible. It is difficult to rinse the last traces of chlorine from the walls of the bomb, and the tendency for residual chlorine to carry over from sample to sample has been observed in a number of laboratories. When a sample high in chlorine has preceded one low in chlorine content, the test on the low-chlorine sample should be repeated, and one or both of the low values thus obtained should be considered suspect if they do not agree within the limits of repeatability of this method.

NOTE: Do not use more than 1 g total of sample and white oil or other chlorine-free combustible material. Use of excess amounts of these materials could cause a buildup of dangerously high pressure and possible rupture of the bomb.

7.1.2 Addition of oxygen. Place the sample cup in position and arrange the thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in Table 1.

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[1]Emery Polishing Paper grit No. 2/0 may be purchased from the Behr-Manning Co., Troy, NY.

[2]Chromic oxide may be purchased from J.T. Baker & Co., Phillipsburg, NJ.

NOTE: Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tiled.

7.1.3 Combustion. Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least 10 minutes. Release the pressure at a slow, uniform rate such that the operation requires at least 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before using it again.

7.1.4 Collection of halogen solution. Using reagent water and a funnel, thoroughly rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover into a 100-mL volumetric flask. Dilute to the mark with reagent water.

7.1.5 Cleaning procedure for bomb and sample cup. Remove any residual fuse wire from the terminals and the cup. Using hot water, rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover. (If any residue remains, first scrub the bomb with Alconox solution). Copiously rinse the bomb, cover, and cup with reagent water.

7.2 Sample Analysis. Analyze the combustate for chlorine or other halogens using the methods listed in Step 2.2. It may be necessary to dilute the samples so that the concentration will fall within the range of standards.

7.3 Calculations. Calculate the concentrations of each element detected in the sample according to the following equation:

$$C_o = \frac{C_{com} \times V_{com} \times DF}{W_o} \qquad (1)$$

where:

C_o = concentration of element in the sample, µg/g
C_{com} = concentration of element in the combustate, µg/mL
V_{com} = total volume of combustate, mL
DF = dilution factor
W_o = weight of sample combusted, g.

Report the concentration of each element detected in the sample in micrograms per gram.

Example: A 0.5-g oil sample was combusted, yielding 10 mL of combustate. The combustate was diluted to 100 mL total volume and analyzed for chloride, which was measured to be 5 µg/mL. The concentration of chlorine in the original sample is then calculated as shown below:

$$C_o = \frac{\frac{5\ \mu g}{mL} \times (10\ mL) \times (10)}{0.5\ g} \qquad (2)$$

$$C_o = 1{,}000\ \frac{\mu g}{g} \qquad (3)$$

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be bombed twice. The results should agree to within 10%, expressed as the relative percent difference of the results.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with the elements of interest at a level commensurate with the levels being determined. The spiked compounds should be similar to those expected in the sample. Any sample suspected of containing > 25% water should also be spiked with organic chlorine.

8.4 For higher levels (e.g., percent levels), spiking may be inappropriate. For these cases, samples of known composition should be combusted. The results should agree to within 10% of the expected result.

8.5 Quality control for the analytical method(s) of choice should be followed.

9.0 PERFORMANCE

See analytical methods referenced in Step 2.2.

10.0 REFERENCES

1. ASTM Method D 808-81, Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method). 1988 Annual Book of ASTM Standards. Volume 05.01 Petroleum Products and Lubricants.

2. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
GAGE PRESSURES

Capacity of bomb, mL	Minimum gage pressure[a], atm	Maximum gage pressure[a], atm
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

[a]The minimum pressures are specified to provide sufficient oxygen for complete combustion, and the maximum pressures represent a safety requirement. Refer to manufacturers' specifications for appropriate gage pressure, which may be lower than those listed here.

APPENDIX

A1. PRECAUTIONARY STATEMENTS

A1.1 Oxygen

Warning--Oxygen vigorously accelerates combustion.

Keep oil and grease away. Do not use oil or grease on regulators, gages, or control equipment.

Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder. Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

For technical use only. Do not use for inhalation purposes.

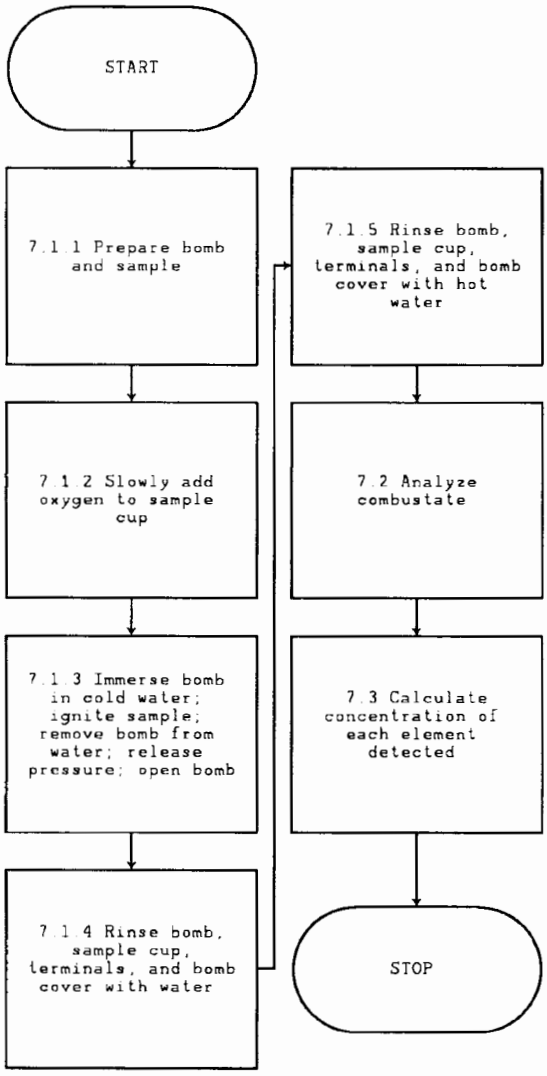
Keep cylinder out of sun and away from heat.

Keep cylinders from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

See Compressed Gas Association booklets G-4 and G4.1 for details of safe practice in the use of oxygen.


START
7.1.1 Prepare bomb and sample
7.1.2 Slowly add oxygen to sample cup
7.1.3 Immerse bomb in cold water; ignite sample; remove bomb from water; release pressure; open bomb
7.1.4 Rinse bomb, sample cup, terminals, and bomb cover with water
7.1.5 Rinse bomb, sample cup, terminals, and bomb cover with hot water
7.2 Analyze combustate
7.3 Calculate concentration of each element detected
STOP

METHOD 6010B

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Refer to Chapter Three for the appropriate digestion procedures.

1.2 Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits for the elements in clean aqueous matrices. The instrument detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements and matrices other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 8.0) is demonstrated.

1.3 Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background

intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

3.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

3.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

3.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction **require** the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement

correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

3.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary.

3.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

3.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

3.1.7 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

3.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

3.1.9 When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

3.1.10 When interelement corrections are <u>not</u> used, verification of absence of interferences is required.

3.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

3.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is $\geq$ 20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate

and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers. The test described in Section 8.5.1 will help determine if a physical interference is present.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

3.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

3.5 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

3.6 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio-frequency generator compliant with FCC regulations.

4.1.3 Optional mass flow controller for argon nebulizer gas supply.

4.1.4 Optional peristaltic pump.

4.1.5 Optional Autosampler.

4.1.6 Argon gas supply - high purity.

4.2 Volumetric flasks of suitable precision and accuracy.

4.3 Volumetric pipets of suitable precision and accuracy.

5.0 REAGENTS

5.1 Reagent or trace metals grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.1.3 Nitric acid (conc), HNO_3.

5.1.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriately sized beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

Note: This section does not apply when analyzing samples that have been prepared by Method 3040.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

For metals:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

For metal salts:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1:1) HCl and 1.0 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1-liter flask, add an additional 10.0 mL of (1:1) HCl and dilute to volume with reagent water.

NOTE: Weight of analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4 % error for some of the compounds.

5.3.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 2.6673 g $K(SbO)C_4H_4O_6$ (element fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.3203 g of As_2O_3 (element fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.5163 g $BaCl_2$ (element fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 µg Be: Do not dry. Dissolve 19.6463 g $BeSO_4{\cdot}4H_2O$ (element fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Boron solution, stock, 1 mL = 1000 µg B: Do not dry. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1-L volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass volumetric container. Use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

5.3.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.1423 g CdO (element fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a

minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.4969 g $CaCO_3$ (element Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.9231 g CrO_3 (element fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.2564 g CuO (element fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.4298 g Fe_2O_3 (element fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.5985 g $Pb(NO_3)_2$ (element fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.3248 g lithium carbonate (element fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.6584 g MgO (element fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Mercury solution, stock, 1 mL = 1000 µg Hg: Do not dry, highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1-L volumetric flask with reagent water.

5.3.18 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.7325 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (element fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Phosphate solution, stock, 1 mL = 1000 µg P: Dissolve 4.3937 g anhydrous KH_2PO_4 (element fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.9069 g KCl (element fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Selenium solution, stock, 1 mL = 1000 µg Se: Do not dry. Dissolve 1.6332 g H_2SeO_3 (element fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Silica solution, stock, 1 mL = 1000 µg SiO_2: Do not dry. Dissolve 2.964 g NH_4SiF_6, weighed accurately to at least four significant figures, in 200 mL (1:20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.

5.3.24 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.5748 g $AgNO_3$ (element fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO_3. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.5419 g NaCl (element fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 2.4154 g of strontium nitrate ($Sr(NO_3)_2$) (element fraction Sr = 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.27 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.3034 g $TlNO_3$ (element fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.28 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least 4 significant figures, in 200 mL (1:1) HCl with heating to effect dissolution. Let solution cool and dilute with (1:1) HCl in a 1-L volumetric flask.

5.3.29 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 2.2957 g NH_4VO_3 (element fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.30 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.2447 g ZnO (element fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Some typical calibration standard combinations are listed in Table 3.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

5.5 Two types of blanks are required for the analysis for samples prepared by any method other than 3040. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations (see Sections 7.3 and 7.4).

5.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The Initial Calibration Verification (ICV) is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard and at concentrations within the linear working range of the instrument (see Section 8.6.1 for use).

5.7 The Continuing Calibration Verification (CCV)) should be prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid-point of the calibration curve (see Section 8.6.1 for use).

5.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards**.** Solubilization and digestion procedures are presented in Sample Preparation Methods (Chapter Three, Inorganic Analytes).

7.2 Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer.

7.2.1 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.

7.2.2 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for

a task. Operating conditions for aqueous solutions usually vary from 1100 to 1200 watts forward power, 14 to 18 mm viewing height, 15 to 19 liters/min argon coolant flow, 0.6 to 1.5 L/min argon nebulizer flow, 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. For an axial plasma, the conditions will usually vary from 1100-1500 watts forward power, 15-19 liters/min argon coolant flow, 0.6-1.5 L/min argon nebulizer flow, 1-1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 second per wavelength peak for sequential instruments and 10 seconds per sample for simultaneous instruments. Reproduction of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively, by adjusting the argon aerosol flow has been recommended as a way to achieve repeatable interference correction factors.

7.2.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

7.2.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a 1000 ug/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. Record the nebulizer gas flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.

7.2.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow.

7.2.3.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure can be used for both horizontal and vertical optimization in the radial mode, but is written for vertical. Aspirate a solution containing 10 ug/L of several selected elements. These elements can be As, Se, Tl or Pb as the least sensitive of the elements and most needing to be optimize or others representing analytical judgement (V, Cr, Cu, Li and Mn are also used with success). Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least

sensitive element. For optimization in the axial mode, follow the instrument manufacturer's instructions.

7.2.3.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.

7.2.3.5 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and viewing height should be re-optimized.

7.2.3.6 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± one reporting limit from zero. The upper control limit is the analyte instrument detection limit. Once established the entire routine must be periodically verified every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine should be kept on file. Special cases where continual verification is required are described elsewhere.

7.2.3.7 Before daily calibration and after the instrument warmup period, the nebulizer gas flow rate must be reset to the determined optimized flow. If a mass flow controller is being used, it should be set to the recorded optimized flow rate, In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same (< 2% change) from day to day.

7.2.4 For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements.

7.2.5 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

7.2.5.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit. Refer to Chapter One for additional guidance on the performance of MDL studies.

7.2.5.2 Determination of limits using reagent water represent a best case situation and do not represent possible matrix effects of real world samples.

7.2.5.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate. Successful analysis of samples with added analytes or using method of standard additions can give confidence in the method detection limit values determined in reagent water.

7.2.5.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the range. One of these should be near the upper limit of the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst should also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges should be determined whenever there is a significant change in instrument response. For those analytes that periodically approach the upper limit, the range should be checked every six months. For those analytes that are known interferences, and are present at above the linear range, the analyst should ensure that the interelement correction has not been inaccurately applied.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and should be checked whenever there have been moderate equipment changes.

7.2.6 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 5.4. Flush the system with the calibration blank (Section 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve must consist of a minimum of a blank and a standard.

7.4 For all analytes and determinations, the laboratory must analyze an ICV (Section 5.6), a calibration blank (Section 5.5.1), and a continuing calibration verification (CCV) (Section 5.7) immediately following daily calibration. A calibration blank and either a calibration verification (CCV) or an ICV must be analyzed after every tenth sample and at the end of the sample run. Analysis of

the check standard and calibration verification must verify that the instrument is within ± 10% of calibration with relative standard deviation < 5% from replicate (minimum of two) integrations. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV or check standard must be reanalyzed. The analysis data of the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

7.5 Rinse the system with the calibration blank solution (Section 5.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.

7.7 The MSA should be used if an interference is suspected or a new matrix is encountered. When the method of standard additions is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for the unfortified aliquot by the volume (Liters) and concentration (mg/L or mg/kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volume (Liters) of the sample aliquot for the denominator. The quotient is the sample concentration.

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution.

NOTE: Refer to Method 7000 for a more detailed discussion of the MSA.

7.8 An alternative to using the method of standard additions is the internal standard technique. Add one or more elements not in the samples and verified not to cause an interelement spectral interference to the samples, standards and blanks; yttrium or scandium are often used. The concentration should be sufficient for optimum precision but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences especially in high solids matrices.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. All quality control measures described in Chapter One should be followed.

8.2 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample (refer to Chapter One).

8.4 Analyze matrix spiked duplicate samples at a frequency of one per matrix batch. A matrix duplicate sample is a sample brought through the entire sample preparation and analytical process in duplicate.

8.4.1.1 The relative percent difference between spiked matrix duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

(A control limit of ± 20% RPD or within the documented historical acceptance limits for each matrix shall be used for sample values greater than ten times the instrument detection limit.)

8.4.1.2 The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Sections 8.5.1 and 8.5.2, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate QC samples as follows.

8.6.1 Verify calibration with the Continuing Calibration Verification (CCV) Standard immediately following daily calibration, after every ten samples, and at the end of an analytical run. Check calibration with an ICV following the initial calibration (Section 5.6). At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV should be at a concentration near the mid-point of the calibration curve. Use a calibration blank (Section 5.5.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.

8.6.1.1 The results of the ICV and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.2 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.1.3 The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

8.6.2 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing the interference check sample (Section 5.8). Results should be within ± 20% of the true value.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 Performance data for aqueous solutions and solid samples from a multilaboratory study (9) are provided in Tables 5 and 6.

10.0 REFERENCES

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TABLE 1
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection Element	Wavelength[a] (nm)	Estimated IDL[b] (µg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227x2	17
Molybdenum	202.030	5.3
Nickel	231.604x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856x2	1.2

[a]The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted (e.g., in the case of an interference) if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are provided as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

TABLE 2
POTENTIAL INTERFERENCES
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM
INTERFERENCE AT THE 100-mg/L LEVEL[c]

Analyte	Wavelength (nm)	Interferant[a,b] Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al -	1000 mg/L	Mg -	1000 mg/L
Ca -	1000 mg/L	Mn -	200 mg/L
Cr -	200 mg/L	Tl -	200 mg/L
Cu -	200 mg/L	V -	200 mg/L
Fe -	1000 mg/L		

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

TABLE 3
MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni,Li, and Sr
V	Ag (see “NOTE” to Section 5.4), Mg, Sb, and Tl
VI	P

TABLE 4. ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1				Sample No. 2				Sample No. 3			
	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b]	Accuracy[d] (%)	True Conc. (ug/L)	Mean Conc. (ug/L)	RSD[b] (%)	Accuracy[d] (%)
Be	750	733	6.2	98	20	20	9.8	100	180	176	5.2	98
Mn	350	345	2.7	99	15	15	6.7	100	100	99	3.3	99
V	750	749	1.8	100	70	69	2.9	99	170	169	1.1	99
As	200	208	7.5	104	22	19	23	86	60	63	17	105
Cr	150	149	3.8	99	10	10	18	100	50	50	3.3	100
Cu	250	235	5.1	94	11	11	40	100	70	67	7.9	96
Fe	600	594	3.0	99	20	19	15	95	180	178	6.0	99
Al	700	696	5.6	99	60	62	33	103	160	161	13	101
Cd	50	48	12	96	2.5	2.9	16	116	14	13	16	93
Co	700	512	10	73	20	20	4.1	100	120	108	21	90
Ni	250	245	5.8	98	30	28	11	93	60	55	14	92
Pb	250	236	16	94	24	30	32	125	80	80	14	100
Zn	200	201	5.6	100	16	19	45	119	80	82	9.4	102
Se[c]	40	32	21.9	80	6	8.5	42	142	10	8.5	8.3	85

[a] Not all elements were analyzed by all laboratories.
[b] RSD = relative standard deviation.
[c] Results for Se are from two laboratories.
[d] Accuracy is expressed as the mean concentration divided by the true concentration times 100.

TABLE 5

ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS[a]

Element	Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Accuracy[c] (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	6	9.1	100
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

[a]these performance values are independent of sample preparation because the labs analyzed portions of the same solutions

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.

TABLE 6

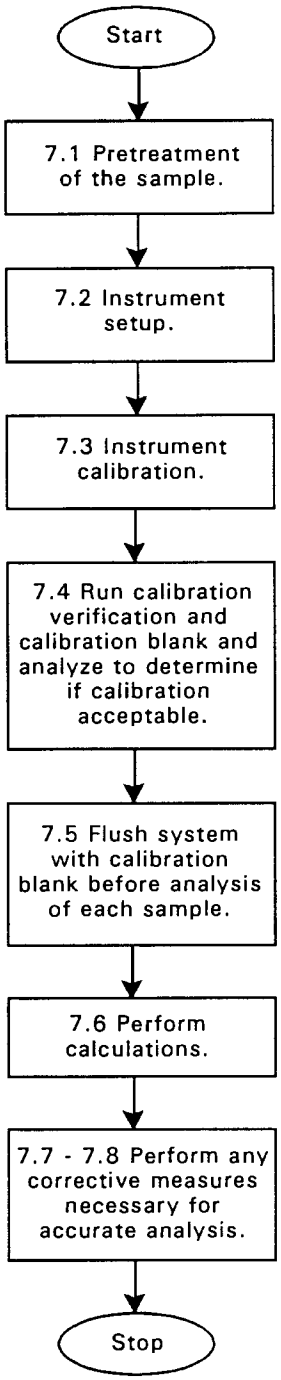
ICP-AES PRECISION AND BIAS FOR SOLID WASTE DIGESTS[a]

Element	Spiked Coal Fly Ash (NIST-SRM 1633a) Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)	Spiked Electroplating Sludge Mean Conc. (mg/L)	N[b]	RSD[b] (%)	Bias[c] (%AAS)
Al	330	8	16	104	127	8	13	110
Sb	3.4	6	73	96	5.3	7	24	120
As	21	8	83	270	5.2	7	8.6	87
Ba	133	8	8.7	101	1.6	8	20	58
Be	4.0	8	57	460	0.9	7	9.9	110
Cd	0.97	6	5.7	101	2.9	7	9.9	90
Ca	87	6	5.6	208	954	7	7.0	97
Cr	2.1	7	36	106	154	7	7.8	93
Co	1.2	6	21	94	1.0	7	11	85
Cu	1.9	6	9.7	118	156	8	7.8	97
Fe	602	8	8.8	102	603	7	5.6	98
Pb	4.6	7	22	94	25	7	5.6	98
Mg	15	8	15	110	35	8	20	84
Mn	1.8	7	14	104	5.9	7	9.6	95
Mo	891	8	19	105	1.4	7	36	110
Ni	1.6	6	8.1	91	9.5	7	9.6	90
K	46	8	4.2	98	51	8	5.8	82
Se	6.4	5	16	73	8.7	7	13	101
Ag	1.4	3	17	140	0.75	7	19	270
Na	20	8	49	130	1380	8	9.8	95
Tl	6.7	4	22	260	5.0	7	20	180
V	1010	5	7.5	100	1.2	6	11	80
Zn	2.2	6	7.6	93	266	7	2.5	101

[a]These performance values are independent of sample preparation because the labs analyzed portions of the same digests.

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.


Start
7.1 Pretreatment of the sample.
7.2 Instrument setup.
7.3 Instrument calibration.
7.4 Run calibration verification and calibration blank and analyze to determine if calibration acceptable.
7.5 Flush system with calibration blank before analysis of each sample.
7.6 Perform calculations.
7.7 - 7.8 Perform any corrective measures necessary for accurate analysis.
Stop

METHOD 6020

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests [1,2]. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of Method 6020 in a multi-laboratory study on solid wastes are listed in Table 1. Acceptability of the method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectroscopy or inductively coupled plasma-atomic emission spectroscopy. It should be noted that the multi-laboratory study was conducted in 1986. Multi-laboratory performance data for the listed elements (and others) are provided in Section 9. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, detection limits will generally be below 0.02 µg/L.

1.3 If Method 6020 is used to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the Method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Section 8.4).

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

1.5 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho,and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant amounts of the recommended internal standards.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total ("acid-leachable") values must be digested using appropriate sample preparation methods (such as Methods 3005 - 3051).

2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 INTERFERENCES

3.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isoptope, or use of another method.

3.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature [3,4]. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature [5], the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal):

> corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =
>
> (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),
> (where the final term adjusts for any selenium contribution at 77 m/z),
>
> NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [6]).

Similarly,

corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =

(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are **ONLY** illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found [7] to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferant. This type of correction has been reported [7] for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas have been shown to greatly reduce molecular interferences [8]. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

3.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement [9]. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended [10] to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes [11]. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

3.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample

deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled plasma-mass spectrometer:

4.1.1 A system capable of providing resolution, better than or equal to amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

4.1.2 Argon gas supply: high-purity grade (99.99%).

5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used [3,4]. Concentrations of antimony and silver between 50-500 µg/L require 1% (v/v) HCl for stability; for concentrations above 500 µg/L Ag, additional HCl will be needed.

5.2 Reagent water: All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity). See Method 6010A, Section 5.3, for instructions on preparing standard solutions from solids.

5.3.1 Bismuth internal standard solution, stock, 1 mL = 100 µg Bi: Dissolve 0.1115 g Bi_2O_3 in a minimum amount of dilute HNO_3 . Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.2 Holmium internal standard solution, stock, 1 mL = 100 µg Ho: Dissolve 0.1757 g $Ho_2(CO_3)_2{\cdot}5H_2O$ in 10 mL reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to d egas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.3 Indium internal standard solution, stock, 1 mL = 100 µg In: Dissolve 0.1000 g indium metal in 10 mL conc. HNO_3. Dilute to 1,000 mL with reagent water.

5.3.4 Lithium internal standard solution, stock, 1 mL = 100 µg ^6Li: Dissolve 0.6312 g 95-atom-% ^6Li, Li_2CO_3 in 10 mL of reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.5 Rhodium internal standard solution, stock, 1 mL = 100 µg Rh: Dissolve 0.3593 g ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL conc. HCl and dilute to 1,000 mL with reagent water.

5.3.6 Scandium internal standard solution, stock, 1 mL = 100 µg Sc: Dissolve 0.15343 g Sc_2O_3 in 10 mL (1+1) hot HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.7 Terbium internal standard solution, stock, 1 mL = 100 µg Tb: Dissolve 0.1828 g $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.8 Yttrium internal standard solution, stock, 1 mL = 100 µg Y: Dissolve 0.2316 g $Y_2(CO_3)_3 \cdot 3H_2O$ in 10 mL (1+1) HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.9 Titanium solution, stock, 1 mL = 100 µg Ti: Dissolve 0.4133 g $(NH_4)_2TiF_6$ in reagent water. Add 2 drops conc. HF and dilute to 1,000 mL with reagent water.

5.3.10 Molybdenum solution, stock, 1 mL = 100 µg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in reagent water. Dilute to 1,000 mL with reagent water.

5.4 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold.) Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^6Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, and ^{209}Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard (see Section 5.7) and monitored weekly for stability.

5.5 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The preparation blank is used to monitor for possible contamination resulting from

the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

5.5.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1 percent HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Section 5.1

5.5.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

5.5.3 The rinse blank consists of 1 to 2 percent HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

NOTE: The ICS solutions in Table 2 are intended to evaluate corrections for known interferences on only the analytes in Table 1. If Method 6020 is used to determine an element not listed in Table 1, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see section 8.4).

5.6 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

5.6.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

5.6.1.1 Mixed ICS solution I may be prepared by adding 13.903 g $Al(NO_3)_3 \cdot 9H_2O$, 2.498 g $CaCO_3$ (dried at 180 C for 1 h before weighing), 1.000 g Fe, 1.658 g MgO, 2.305 g Na_2CO_3, and 1.767 g K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

5.6.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g 85 % H_3PO_4, 6.373 g 96% H_2SO_4, 40.024 g 37% HCl, and 10.664 g citric acid $C_6O_7H_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

5.6.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100-µg/mL arsenic, cadmium, chromium, cobalt, copper, manganese, nickel, silver, and zinc stock solutions to about

50 mL reagent water. Add 2.0 mL concentrated HNO_3, and dilute to 100.0 mL with reagent water.

5.6.1.4 Working ICS Solutions

5.6.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (5.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), and 5.0 mL of mixed ICS solution II (5.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

5.6.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (5.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), 5.0 mL of mixed ICS solution II (5.7.1.2), and 2.0 mL of Mixed ICS solution III (5.7.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

5.7 The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

5.8 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 7.5). This solution is also used to verify that the instrument has reached thermal stability (See Section 7.4).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection procedures should address the considerations described in Chapter Nine of this Manual.

6.2 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1.3 for information on sample handling and preservation. Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in Method 6020.

7.0 PROCEDURE

7.1 Solubilization and digestion procedures are presented in the Sample Preparation Methods (e.g., Methods 3005 - 3051).

7.2 Initiate appropriate operating configuration of the instruments computer according to the instrument manufacturer's instructions.

7.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

7.4 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 5.8) at least four times with relative standard deviations of $\leq$ 5% for the analytes contained in the tuning solution.

> NOTE: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

7.5 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10 percent peak height.

7.6 Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Table 1 are provided in Table 3), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Flush the system with the rinse blank (5.5.3) between each standard solution. Use the average of at leastthree integrations for both calibration and sample analyses.

7.7 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are liste in Table 3.

7.8 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the calibration verification solution (Section 5.7). When measurements exceed ± 10% of the accepted value, the analyses must be terminated, the problem corrected, the instrument recalibrated, and the new calibration verified. Any samples analyzed under an out-of-control calibration must be reanalyzed. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift. A recalibration must then be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed.

7.9 Flush the system with the rinse blank solution (5.5.3) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample (see Section 7.7). Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (Section 5.6) and the calibration blank (Section 5.5.1) at a frequency of at least once every 10 analytical samples. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

7.10 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 7.6 and 7.8).

7.11 Calculations: The quantitative values shall be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.

7.11.1 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations should include appropriate interference corrections (see Section 3.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and be available for easy reference or inspection.

8.2 Instrument Detection Limits (IDLs) in µg/L can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept with the instrument log book. Refer to Chapter One for additional guidance.

8.3 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard, the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal-standard intensities fall within the prescribed window. The intensity levels of the internal standards for the calibration blank (Section 5.5.1) and instrument check standard (Section 5.6) must agree within ± 20 percent of the intensity level of the internal standard of the original calibration solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

8.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correcttion equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Section 3.2) for each instrument system are acceptable corrections for use in Method 6020.

8.5 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, refer to Section 5.5.2), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected. One dilution test must be included for each twenty samples (or less) of each matrix in a batch.

8.6 Post-Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect (Refer to Method 7000).

8.7 A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.

8.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:

8.8.1 Check instrument calibration using a calibration blank (Section 5.5.1) and the initial calibration verification solution (Sections 5.7 and 7.9).

8.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard (Section 5.6) and the calibration blank (Section 5.5.1). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

8.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within ± 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed .

8.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. If the laboratory consistently has concentrations greater than 3 times the IDL, the IDL may be indicative of an estimated IDL and should be re-evaluated.

8.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to Section 3.0 for a discussion on intereferences and potential solutions to those intereferences if additional guidance is needed.

8.10 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

8.10.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

9.0 METHOD PERFORMANCE

9.1 In an EPA multi-laboratory study, 10 laboratories applied the ICP-MS technique to both aqueous and solid samples. TABLE 4 summarizes the method performance data for aqueous samples. Performance data for solid samples is provided in TABLE 5.

10.0 REFERENCES

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TABLE 1. ELEMENTS APPROVED FOR ICP-MS DETERMINATION

Element	CAS* #
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Chromium	7440-47-3
Cobalt	7440-48-4
Copper	7440-50-8
Lead	7439-92-1
Manganese	7439-96-5
Nickel	7440-02-0
Silver	7440-22-4
Thallium	7440-28-0
Zinc	7440-66-6

TABLE 2. RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution component	Solution A Concentration(mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.0200
Cd	0.0	0.0200
Cr	0.0	0.0200
Co	0.0	0.0200
Cu	0.0	0.0200
Mn	0.0	0.0200
Ni	0.0	0.0200
Ag	0.0	0.0200
Zn	0.0	0.0200

TABLE 3. RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Mass	Element of interest
27	Aluminum
121, **123**	Antimony
75	Arsenic
138, 137, 136, **135**, 134	Barium
9	Beryllium
209	Bismuth (IS)
114, 112, **111**, 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium (I)
35, 37, (77, 82)[a]	Chlorine (I)
52, **53**, **50**, 54	Chromium
59	Cobalt
63, **65**	Copper
165	Holmium (IS)
115, 113	Indium (IS)
56, **54**, **57**, 58	Iron (I)
139	Lanthanum (I)
208, **207**, **206**, 204	Lead
6[b], 7	Lithium (IS)
24, **25**, **26**	Magnesium (I)
55	Manganese
98, 96, 92, **97**, 94, (108)[a]	Molybdenum (I)
58, **60**, 62, **61**, 64	Nickel
39	Potassium (I)
103	Rhodium (IS)
45	Scandium (IS)
107, **109**	Silver
23	Sodium (I)
159	Terbium (IS)
205, 203	Thallium
120, **118**	Tin (I)
89	Yttrium (IS)
64, **66**, **68**, **67**, 70	Zinc

NOTE: Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes. [a] These masses are also useful for interference correction (Section 3.2). [b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

TABLE 4. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	12 - 14	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

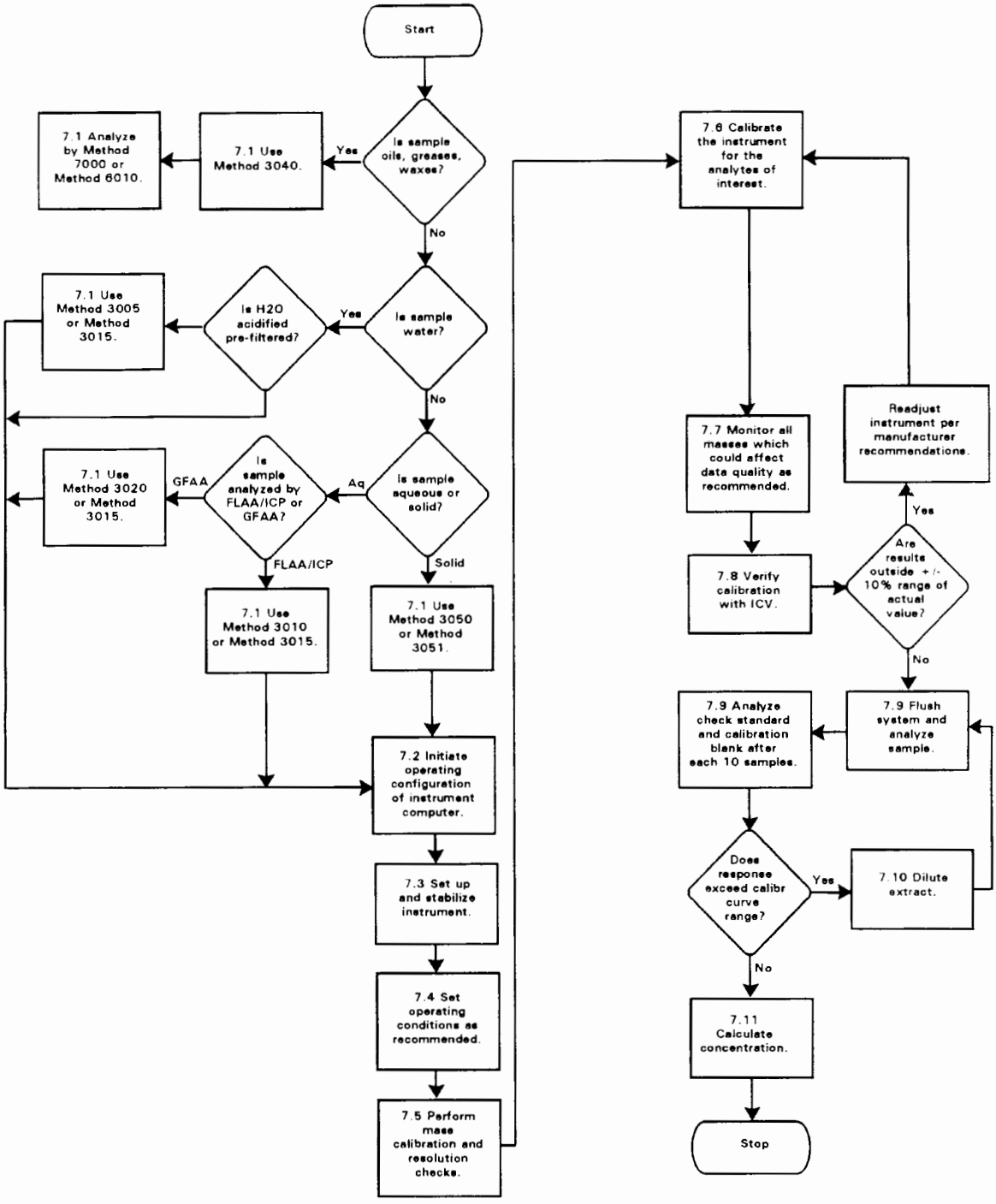
[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. [b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). [c] S is the number of samples with results greater than the limit of quantitation. [d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

TABLE 5. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	4.3 - 17	15 - 16	7
Beryllium	50 - 87	19 - 34	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. [b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). [c] S is the number of samples with results greater than the limit of quantitation. [d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

METHOD 6020
INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY



METHOD 7000A

ATOMIC ABSORPTION METHODS

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes. While drinking water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis for both total and acid leachable metals. Analysis for dissolved elements does not require digestion if the sample has been filtered and acidified.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. For clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. For certain samples, lower concentrations may also be determined using the furnace techniques. The detection limits given in Table 1 are somewhat dependent on equipment (such as the type of spectrophotometer and furnace accessory, the energy source, the degree of electrical expansion of the output signal), and are greatly dependent on sample matrix. Detection limits should be established, empirically, for each matrix type analyzed. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Step 3.2.1) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard additions (see Step 8.7).

1.3 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, reference is made to specialized procedures (in addition to the furnace procedure) such as the gaseous-hydride method for arsenic and selenium and the cold-vapor technique for mercury.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy, the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrix. Solids, slurries, and suspended material must be subjected to

a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Step 3.2 (Sample Preparation Methods).

2.3 In direct-aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.4 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube rather than the flame, the use of smaller sample volumes or detection of lower concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption, except that a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

3.0 INTERFERENCES

3.1 Direct aspiration

3.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

3.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

3.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available, a nonabsorbing wavelength should be checked. Preferably, samples containing high solids should be extracted.

3.1.4 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li or Cs.

3.1.5 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

3.1.6 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.1.7 All metals are not equally stable in the digestate, especially if it contains only nitric acid, not nitric acid and hydrochloric acid. The digestate should be analyzed as soon as possible, with preference given to Sn, Sb, Mo, Ba, and Ag.

3.2 Furnace procedure

3.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique (see Step 8.6) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.

2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see Step 8.7.2).

3.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

3.2.3 Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

3.2.4 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

3.2.5 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

3.2.6 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to nitric acid is required, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

3.2.7 Carbide formation resulting from the chemical environment of the furnace has been observed. Molybdenum may be cited as an example. When carbides form, the metal is released very slowly from the resulting metal carbide as atomization continues. Molybdenum may require 30 seconds or more atomization time before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite. Elements that readily form carbides are noted with the symbol (p) in Table 1.

3.2.8 For comments on spectral interference, see Step 3.1.5.

3.2.9 Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in Step 4.8. Pipet tips are a frequent source of contamination. If suspected, they should be acid soaked with 1:5 nitric acid and rinsed thoroughly with tap and reagent water. The use of a better grade of pipet tip can greatly reduce this problem. Special attention should be given to reagent blanks in both analysis and in the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer - Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a graphical display.

4.2 Burner - The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

4.3 Hollow cathode lamps - Single-element lamps are preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used when available. Other types of lamps meeting the performance criteria of this method may be used.

4.4 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory.

4.5 Graphical display and recorder - A recorder is recommended for furnace work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak shape, etc., can be easily recognized.

4.6 Pipets - Microliter, with disposable tips. Sizes can range from 5 to 100 uL as required. Pipet tips should be checked as a possible source of contamination prior to their use. The accuracy of automatic pipets must be verified daily. Class A pipets can be used for the measurement of volumes larger than 1 mL.

4.7 Pressure-reducing valves - The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

4.8 Glassware - All glassware, polypropylene, or Teflon containers, including sample bottles, flasks and pipets, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first

ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All reagents should be analyzed to provide proof that all constituents are below the MDLs.

5.2 Reagent water. All references to water in this method refer to reagent water unless otherwise specified. Reagent grade water will be of at least 16 Mega Ohm quality.

5.3 Nitric acid (concentrated), HNO_3. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.4 Hydrochloric acid (1:1), HCl. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.5 Fuel and oxidant - High purity acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air and should be clean and dry. Nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

5.6 Stock standard metal solutions - Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic salts using water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used (see Step 8.7).

5.7 Calibration standards - For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorbance of 0.0 to 0.7. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal. Calibration curves are always required.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Metallic Analytes.

7.0 PROCEDURE

7.1 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrices. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three, Step 3.2, Sample Preparation Methods. Samples which are to be analyzed for dissolved constituents need not be digested if they have been filtered and acidified.

7.2 Direct aspiration (flame) procedure

7.2.1 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for a particular instrument. In general, after choosing the proper lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes, unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability. Balance the photometer. Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

7.3 Furnace procedure

7.3.1 Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of a particular instrument.

7.3.2 Background correction is important when using flameless atomization, especially below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Zeeman background correction is effective in overcoming composition or structured background

interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

7.3.3 Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected through blank burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.

7.3.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.3.5 To verify the absence of interference, follow the serial dilution procedure given in Step 8.6.

7.3.6 A check standard should be run after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

7.4 Calculation

7.4.1 For determination of metal concentration by direct aspiration and furnace: Read the metal value from the calibration curve or directly from the read-out system of the instrument.

7.4.2 If dilution of sample was required:

$$\text{ug/L metal in sample} = A \left(\frac{C + B}{C}\right)$$

where:

A = ug/L of metal in diluted aliquot from calibration curve.
B = Acid blank matrix used for dilution, mL.
C = Sample aliquot, mL.

7.4.3 For solid samples, report all concentrations in consistent units based on wet weight. Hence:

$$\text{ug metal/kg sample} = \frac{A \times V}{W}$$

where:

A = ug/L of metal in processed sample from calibration curve.
V = Final volume of the processed sample, mL.
W = Weight of sample, grams.

7.4.4 Different injection volumes must not be used for samples and standards. Instead, the sample should be diluted and the same size injection volume be used for both samples and standards. If dilution of the sample was required:

$$\text{ug/L of metal in sample} = Z \left(\frac{C + B}{C} \right)$$

where:

Z = ug/L of metal read from calibration curve or read-out system.
B = Acid blank matrix used for dilution mL.
C = Sample aliquot, mL.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. After calibration, the calibration curve must be verified by use of at least a calibration blank and a calibration check standard (made from a reference material or other independent standard material) at or near the mid-range. The calibration reference standard must be measured within 10 % of it's true value for the curve to be considered valid.

8.3 If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a mid-range standard or reference standard after every 10 samples. This sample value must be within 20% of the true value, or the previous ten samples need to be reanalyzed.

8.4 At least one matrix spike and one matrix spike duplicate sample shall be included in each analytical batch. A laboratory control sample shall also be processed with each sample batch. Refer to Chapter One for more information.

8.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) is recommended (see Section 8.7 below). Section 8.6 provides tests to evaluate the need for using the MSA.

8.6 Interference tests

8.6.1 Dilution test - For each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. Determine the apparent concentration in the undiluted sample. Dilute the sample by a minimum of five fold (1+4) and reanalyze. If all of the samples in the batch are below 10 times the detection limits, perform the spike recovery analysis described below. Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences, and such samples may be analyzed without using the method of standard additions.

8.6.2 Recovery test - If results from the dilution test do not agree, a matrix interference may be suspected and a spiked sample should be analyzed to help confirm the finding from the dilution test. Withdraw another aliquot of the test sample and add a known amount of analyte to bring the concentration of the analyte to 2 to 5 times the original concentration. If all of the samples in the batch have analyte concentrations below the detection limit, spike the selected sample at 20 times the detection limit. Analyze the spiked sample and calculate the spike recovery. If the recovery is less than 85% or greater than 115%, the method of standard additions shall be used for all samples in the batch.

8.7 Method of standard additions - The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The method of standard additions shall be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

8.7.1 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_S of a standard analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

8.7.2 Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled

the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1. A linear regression program may be used to obtain the intercept concentration.

8.7.3 For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

1. The apparent concentrations from the calibration curve must be linear over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.

2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

3. The determination must be free of spectral interference and corrected for nonspecific background interference.

8.8 All quality control measures described in Chapter One should be followed.

9.0 METHOD PERFORMANCE

9.1 See individual methods.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
ATOMIC ABSORPTION CONCENTRATION RANGES

Metal	Direct Aspiration		Furnace Procedure[a,c]
	Detection Limit (mg/L)	Sensitivity (mg/L)	Detection Limit (ug/L)
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic[b]	0.002	--	1
Barium	0.1	0.4	2
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	1
Iron	0.03	0.12	1
Lead	0.1	0.5	1
Lithium	0.002	0.04	--
Magnesium	0.001	0.007	--
Manganese	0.01	0.05	0.2
Mercury[d]	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel	0.04	0.15	--
Osmium	0.03	1	--
Potassium	0.01	0.04	--
Selenium[b]	0.002	--	2
Silver	0.01	0.06	0.2
Sodium	0.002	0.015	--
Strontium	0.03	0.15	--
Thallium	0.1	0.5	1
Tin	0.8	4	--
Vanadium(p)	0.2	0.8	4
Zinc	0.005	0.02	0.05

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

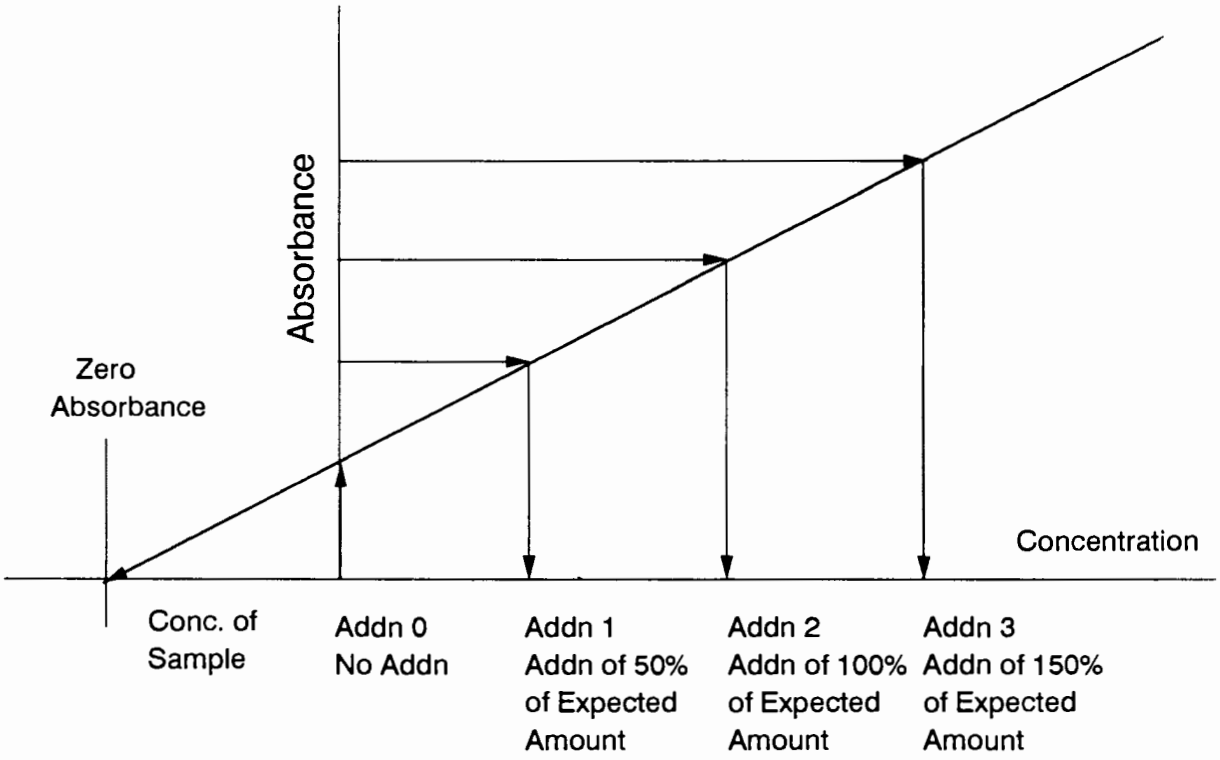
[a]For furnace sensitivity values, consult instrument operating manual.

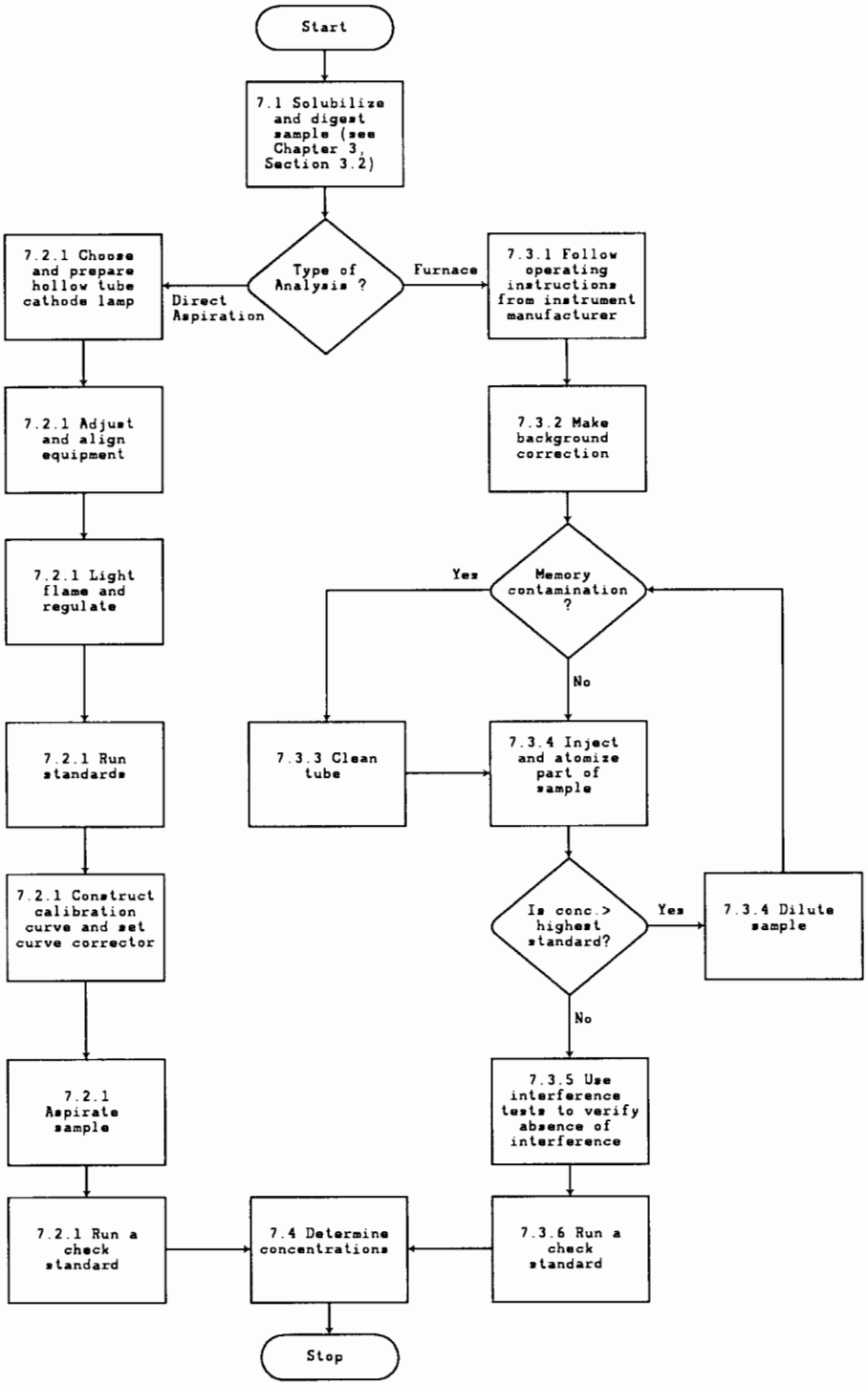
[b]Gaseous hydride method.

[c]The listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

[d]Cold vapor technique.

FIGURE 1.
STANDARD ADDITION PLOT




Start
7.1 Solubilize and digest sample (see Chapter 3, Section 3.2)
Type of Analysis ?
Direct Aspiration
Furnace
7.2.1 Choose and prepare hollow tube cathode lamp
7.2.1 Adjust and align equipment
7.2.1 Light flame and regulate
7.2.1 Run standards
7.2.1 Construct calibration curve and set curve corrector
7.2.1 Aspirate sample
7.2.1 Run a check standard
7.3.1 Follow operating instructions from instrument manufacturer
7.3.2 Make background correction
Memory contamination ?
Yes
No
7.3.3 Clean tube
7.3.4 Inject and atomize part of sample
Is conc.> highest standard?
Yes
7.3.4 Dilute sample
No
7.3.5 Use interference tests to verify absence of interference
7.3.6 Run a check standard
7.4 Determine concentrations
Stop

METHOD 7020

ALUMINUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Aluminum may be as much as 15% ionized in a nitrous-oxide/acetylene flame. Use of an ionization suppressor (1,000 ug/mL K as KCl) as in Method 7000, Paragraph 3.1.4, will eliminate this interference.

3.3 Aluminum is a very common contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Aluminum hollow cathode lamp.**
4.2.2 **Wavelength:** 324.7 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of aluminum metal in dilute HCl with gentle warming. Dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. Samples and standards should also contain 2 mL KCl/100 mL solution (Paragraph 3.2 above).

5.3 Potassium chloride solution: Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

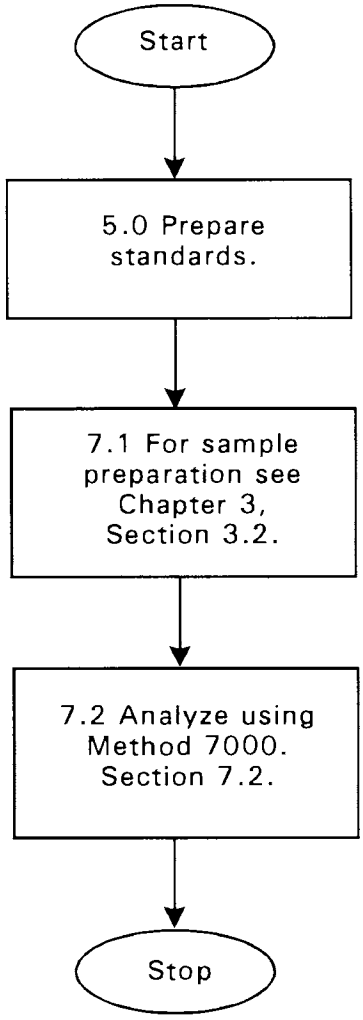
9.1 Precision and accuracy data are available in Method 202.1 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-50 mg/L, with a wavelength of 309.3 nm.
Sensitivity: 1 mg/L.
Detection limit: 0.1 mg/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, Method 202.1, December 1982.


Start
5.0 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000. Section 7.2.
Stop

ANTIMONY (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In the presence of lead (1,000 mg/L), a spectral interference may occur at the 217.6-nm resonance line. In this case, the 231.1-nm antimony line should be used.

3.3 Increasing the acid concentrations decreases the antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards should be matched.

3.4 Excess concentrations of copper and nickel (and possibly other elements), as well as acids, can interfere with antimony analyses. If the sample contains these matrix types, either matrices of the standards should be matched to those of the sample or the sample should be analyzed using a nitrous oxide/acetylene flame.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Antimony hollow cathode lamp or electrodeless discharge lamp.**
4.2.2 **Wavelength:** 217.6 nm (primary); 231.1 nm (secondary).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Fuel lean.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Carefully weigh 2.7426 g of antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ (analytical reagent grade), and dissolve in Type II water. Dilute to 1 liter with Type II water; 1 mL = 1 mg Sb (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should contain 0.2% (v/v) HNO_3 and 1-2% v/v HCl, prepared using the same types of acid and at the same concentrations as in the sample after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for Sb. It yields better recoveries than either Method 3010 or Method 3050. There is no hard digestion for Sb at this time.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration Procedure.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

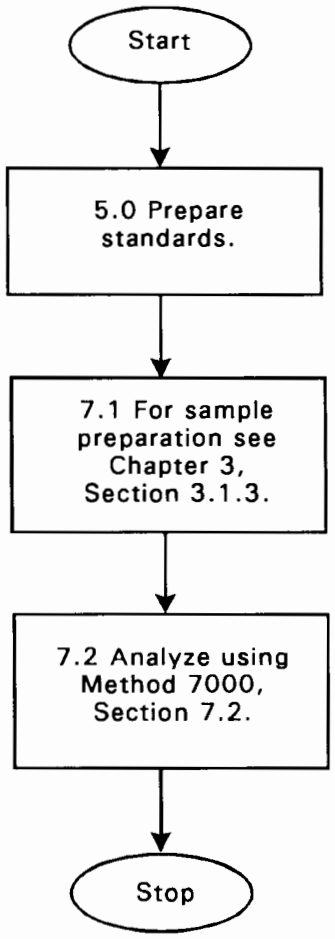
Optimum concentration range: 1-40 mg/L with a wavelength of 217.6 nm.
Sensitivity: 0.5 mg/L.
Detection limit: 0.2 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 5.0 and 15 mg Sb/L gave the standard deviations of $\pm$0.08 and $\pm$0.1, respectively. Recoveries at these levels were 96% and 97%, respectively.

9.3 For concentrations of antimony below 0.35 mg/L, the furnace procedure (Method 7041) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 204.1.


Start
5.0 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.1.3.
7.2 Analyze using Method 7000, Section 7.2.
Stop

ANTIMONY (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High lead concentration may cause a measurable spectral interference on the 217.6-nm line. If this interference is expected, the secondary wavelength should be employed or Zeeman background correction used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 800°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2700°C.
4.2.4 **Purge gas:** Argon or nitrogen.
4.2.5 **Wavelength:** 217.6 nm (primary); 231.1 nm (alternate).
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in Type II water. Dilute to 1 liter with Type II water; 1 mL = 1 mg Sb (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should contain 0.2% (v/v) HNO_3 and 1-2% (v/v) HCl, prepared using the same types of acid and at the same concentrations as in the sample after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for Sb. It yields better recoveries than either Method 3010 or Method 3050. There is no hard digestion for Sb at this time.

NOTE: The addition of HCl acid to the digestate prevents the furnace analysis of this digestate for many other metals.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

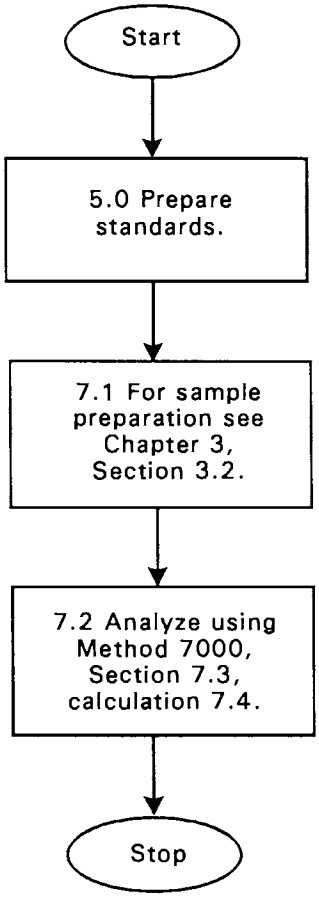
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 20-300 ug/L.
Detection limit: 3 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 204.2.


Start
5.0 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000, Section 7.3, calculation 7.4.
Stop

METHOD 7060A

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during atomization will be proportional to the arsenic concentration. Other modifiers may be used in place of nickel nitrate if the analyst documents the chemical and concentration used.

2.3 The typical detection limit for water samples using this method is 1 ug/L. This detection limit may not be achievable when analyzing waste samples.

3.0 INTERFERENCES

3.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A matrix modifier such as nickel nitrate must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferent in the analysis of arsenic, especially using D_2 arc background

correction. Although Zeeman background correction is very useful in this situation, use of any appropriate background correction technique is acceptable.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beaker or equivalent: 250 mL.

4.2 Class A Volumetric flasks: 10-mL.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a suitable recording device.

4.4 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for arsenic analysis.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Data systems recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank using the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank using the H_2O_2 is <MDL, the reagent can be used.

5.4 Arsenic standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide (As_2O_3, analytical reagent grade) or equivalent in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter (1 mL = 1 mg As).

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in reagent water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with reagent water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3, 30% H_2O_2, and 5% nickel nitrate solution or other appropriate matrix modifier. Amounts added should be representative of the concentrations found in the samples. Dilute to 100 mL with reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid and refrigerated prior to analysis.

6.5 Although waste samples do not need to be refrigerated sample handling and storage must comply with the minimum requirements established in Chapter One.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Paragraphs 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050A. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer a known volume of well-mixed sample to a 250-mL Griffin beaker or equivalent; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat, until digestion is complete, at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool, transfer to a volumetric flask, and bring back to 50 mL with reagent water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution or other appropriate matrix modifier, and dilute to 10 mL with reagent water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The optimal concentration range for aqueous samples using this method is 5-100 ug/L. Concentration ranges for non-aqueous samples will vary with matrix type.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

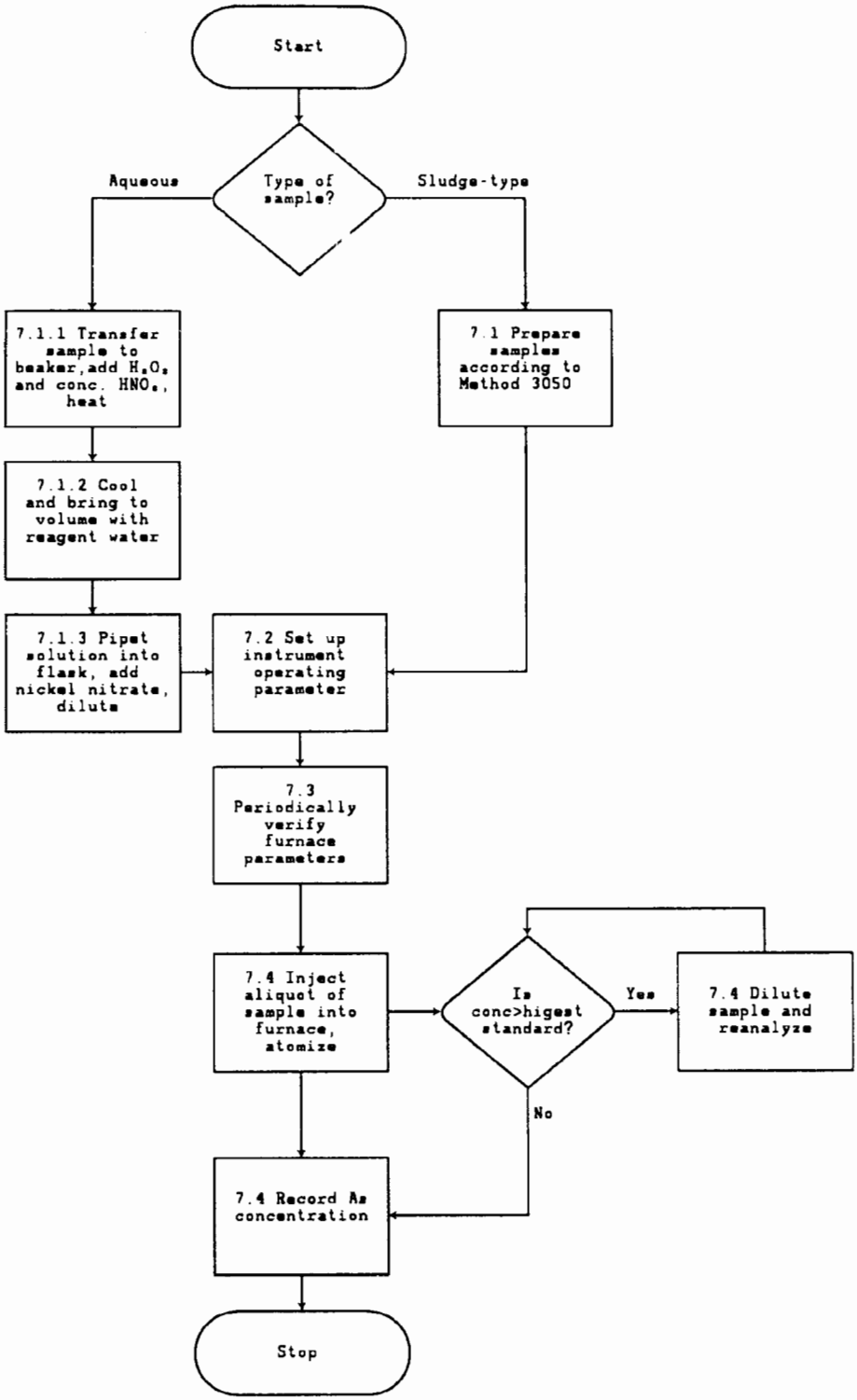
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	2.0, 1.8 ug/g
Oily soil	3050	3.3, 3.8 ug/g
NBS SRM 1646 Estuarine sediment	3050	8.1, 8.33 ug/g[a]
Emission control dust	3050	430, 350 ug/g

[a]Bias of -30 and -28% from expected, respectively.


Start
Type of sample?
Aqueous
Sludge-type
7.1.1 Transfer sample to beaker, add H_2O_2 and conc. HNO_3, heat
7.1.2 Cool and bring to volume with reagent water
7.1.3 Pipet solution into flask, add nickel nitrate, dilute
7.1 Prepare samples according to Method 3050
7.2 Set up instrument operating parameter
7.3 Periodically verify furnace parameters
7.4 Inject aliquot of sample into furnace, atomize
Is conc>higest standard?
Yes
7.4 Dilute sample and reanalyze
No
7.4 Record As concentration
Stop

METHOD 7061A

ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7061 is an atomic absorption procedure for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7061A is approved only for sample matrices that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt, and molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method (Step 7.1). Next, the arsenic in the digestate is reduced to the trivalent form with tin chloride. The trivalent arsenic is then converted to a volatile hydride using hydrogen produced from a zinc/hydrochloric acid reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of sulfur trioxide (SO_3) are observed.

3.3 Elemental arsenic and many of its compounds are volatile; therefore, certain samples may be subject to losses of arsenic during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 Beaker or equivalent - 100-mL.

4.2 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

4.3.1 Medicine dropper - Capable of fitting into a size "0" rubber stopper and delivering 1.5 mL.

4.3.2 Pear-shaped reaction flask - 50-mL, with two 14/20 necks (Scientific Glass JM-5835 or equivalent).

4.3.3 Gas inlet-outlet tube - Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer - To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube - 10-cm, filled with glass to prevent particulate matter from entering the burner.

4.3.6 Flow meter - Capable of measuring 1 liter/min.

4.3.7 Class A volumetric flasks.

4.3.8 Graduated cylinder or equivalent.

4.4 Atomic absorption spectrophotometer - Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner - Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Arsenic hollow cathode lamp or arsenic electrodeless discharge lamp.

4.7 Strip-chart recorder.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interferent free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.4 Sulfuric acid (concentrated), H_2SO_4. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.5 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.6 Diluent - Add 100 mL 18N H_2SO_4 and 400 mL concentrated HCl to 400 mL water and dilute to a final volume of 1 liter with water.

5.7 Potassium iodide solution - Dissolve 20 g KI in 100 mL water.

5.8 Stannous chloride solution - Dissolve 100 g $SnCl_2$ in 100 mL concentrated HCl.

5.9 Arsenic solutions

5.9.1 Arsenic standard solution (1,000 mg/L) - Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide As_2O_3 in 100 mL of water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.9.2 Intermediate arsenic solution - Pipet 1 mL stock arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3/liter (1 mL = 10 ug As).

5.9.3 Standard arsenic solution - Pipet 10 mL intermediate arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3/liter (1 mL = 1 ug As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g. containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of < 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 50-mL aliquot of digested sample (or, in the case of analysis of EP extracts, 50 mL) of the material to be analyzed in a 100-mL beaker. Add 10 mL concentrated HNO_3 and 12 mL 18N H_2SO_4. Evaporate the sample in the hood on an electric hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let the sample char. If charring occurs, immediately turn off the heat, cool, and add an additional 3 mL of HNO_3. Continue to add additional HNO_3 in order to maintain an excess (as evidenced by the formation of brown fumes). Do not let the solution darken, because arsenic may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete. Cool the sample, add about 25 mL water, and again evaporate until SO_3 fumes are produced in order to expel oxides of nitrogen. Cool. Transfer the digested sample to a 100-mL volumetric flask. Add 40 mL of concentrated HCl and bring to volume with water.

7.2 Prepare working standards from the standard arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 ug As/liter.

7.3 If EP extracts are being analyzed or if a matrix interference is encountered, take the 15-, 20-, and 25-mg/liter standards and quantitatively transfer 25 mL of each of these standards into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each flask. Bring to volume with water containing 1.5 mL HCl/liter.

7.4 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with water containing 1.5 mL HCl/liter. This is the zero addition aliquot.

NOTE: The absorbance from the zero addition aliquot will be one-fifth that produced by the prepared sample. The absorbance from the spiked samples will be one-half that produced by the standards plus the contribution from one-fifth of the prepared sample. Keeping these absorbances in mind will assist in judging the correct dilutions to produce optimum absorbance.

7.5 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel and add 1 mL KI solution. Add 0.5 mL $SnCl_2$ solution. Allow at least 10 minutes for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. After the recorder pen begins to return to the base line, the reaction vessel can be removed.

CAUTION: Arsine is very toxic. Precautions must be taken to avoid inhaling arsine gas.

7.6 Use the 193.7-nm wavelength and background correction for the analysis of arsenic.

7.7 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.8 If the method of standard additions was employed, plot the absorbances of spiked samples and blank vs. the concentrations. The extrapolated value will be one-fifth the concentration of the original sample. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration can be part of the calibration curve.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.3 of Methods for Chemical Analysis of Water and Wastes.

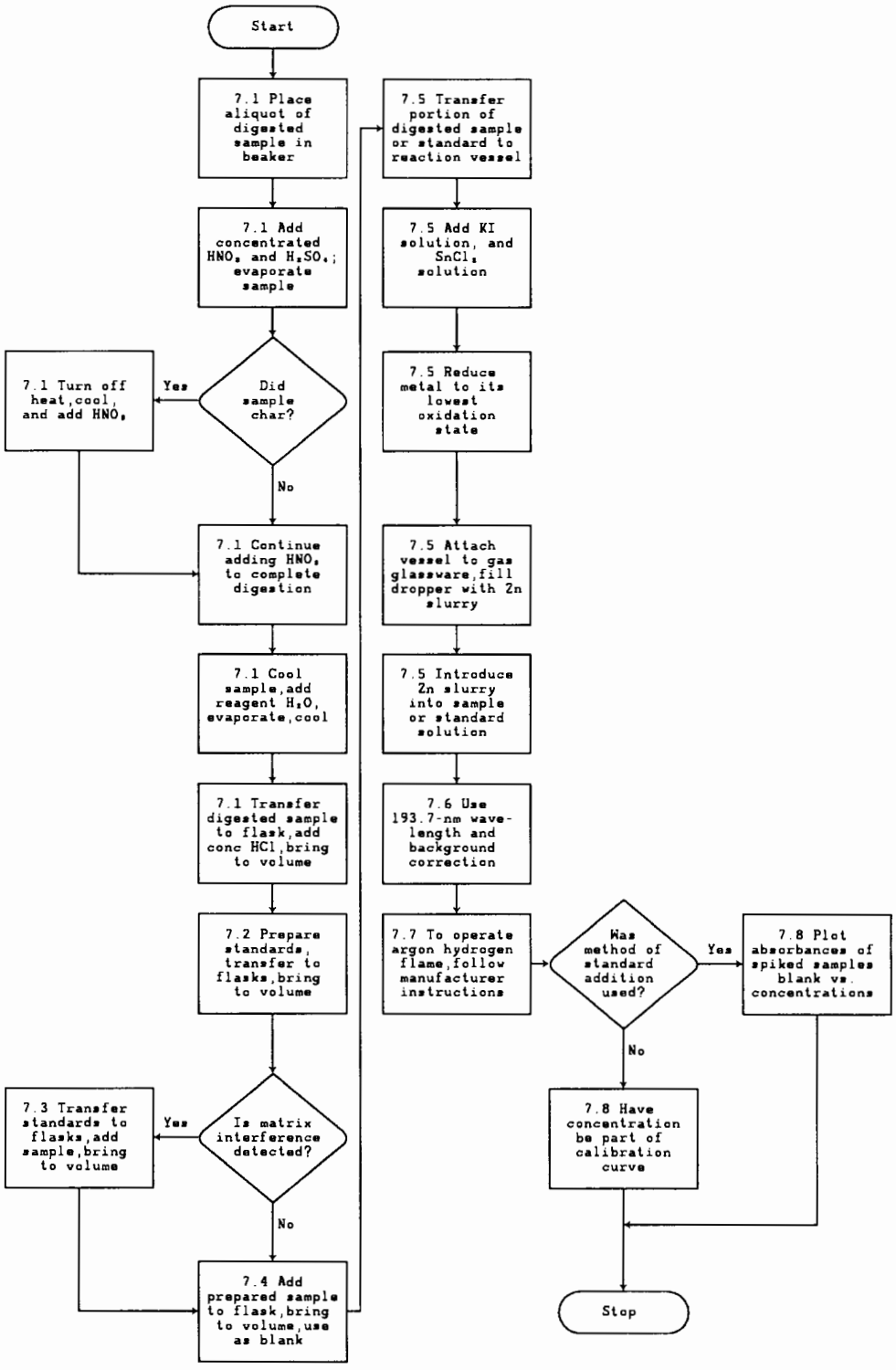
10.0 REFERENCES

1. Methods For Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 7061A
ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)



METHOD 7062

ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7062 is an atomic absorption procedure for determining 1 µg/L to 400 µg/L concentrations of antimony and arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7062 is approved for sample matrices that contain up to a total of 4000 mg/L concentrations of cobalt, copper, iron, mercury, or nickel. A solid sample can contain up to 40% by weight of the interferents before exceeding 4000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are used to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near dryness at the end of the digestion followed by degassing the samples upon addition of urea. L-cysteine is then added as a masking agent. Next, the antimony and arsenic in the digest are reduced to the trivalent forms with potassium iodide. The trivalent antimony and arsenic are then converted to volatile hydrides using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into, and decompose in, a heated quartz cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic or antimony concentration.

2.3 The typical detection limit for this method is 1.0 µg/L.

3.0 INTERFERENCES

3.1 Very high (>4000 mg/L) concentrations of cobalt, copper, iron, mercury, and nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near dryness followed by reaction with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

3.3 Even after acid digestion, organic compounds will remain in the sample. These flame gases and these organic compounds can absorb at the analytical wavelengths and background correction must be used.

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min; and potassium iodide flow = 0.5 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of a fluorocarbon (PFA or TFM) and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater, if appropriate: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting and separating liquid and gaseous products (P.T. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier

gas with the hydrides is dried by passing the gasses through a small (< 25 mL) volume condensor coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter/Regulator: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17 cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with an appropriate recording device.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Antimony and arsenic hollow cathode lamps or antimony and arsenic electrodeless discharge lamps and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water: Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO_3): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H_2O_2): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

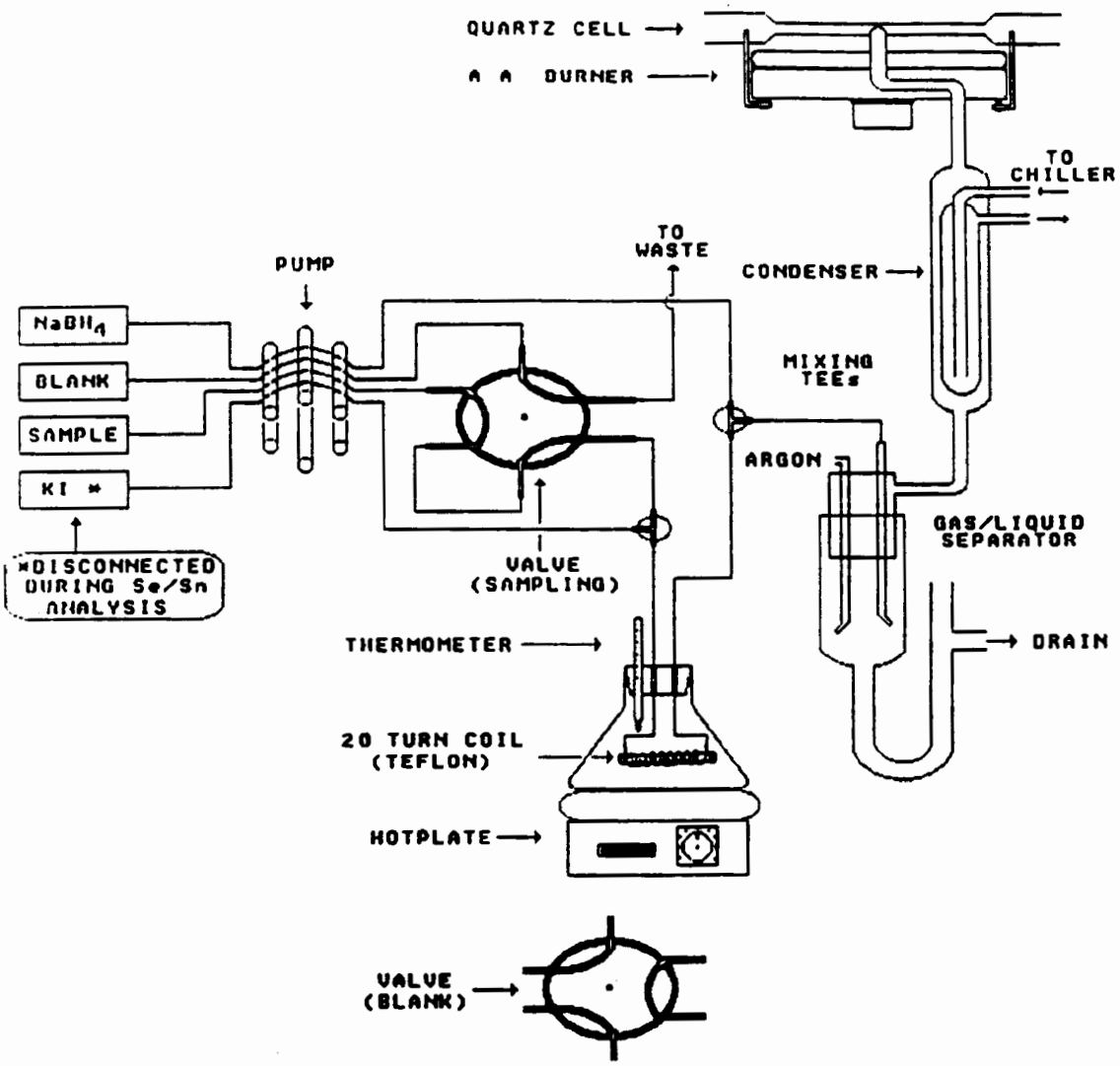


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus set-up and an AAS sample introduction system.

5.6 Urea (H_2NCONH_2): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

5.7 L-cysteine ($C_6H_{12}N_2O_4S_2$): A 1.00-g portion of reagent grade L-cystine must be added to a 25-mL aliquot of each sample for masking the effects of suppressing transition metals (see Section 7.2).

5.8 20% Potassium iodide (KI): A 20% KI solution (20 g reagent-grade KI dissolved and brought to volume in 100 mL reagent water) must be prepared for reduction of antimony and arsenic to their +3 valence states.

5.9 4% Sodium borohydride ($NaBH_4$): A 4% sodium borohydride solution (20 g reagent-grade $NaBH_4$ plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the antimony and arsenic to their hydrides.

5.10 Analyte solutions:

5.10.1 **Antimony and arsenic stock standard solution** (1,000 mg/L): Either procure certified aqueous standards from a supplier and verify by comparison with a second standard, or dissolve 1.197 g of antimony trioxide Sb_2O_3 and 1.320 g of arsenic trioxide As_2O_3 in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.10.2 **Intermediate antimony and arsenic solution:** Pipet 1 mL stock antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter (1 mL = 10 µg each of Sb and As).

5.10.3 **Standard antimony and arsenic solution:** Pipet 10 mL intermediate antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter (1 mL = 1 µg each of Sb and As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile antimony and arsenic compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in antimony recovery; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if analytes are known to exceed 400 µg/L or if interferents are expected to exceed 4000 mg/L in the digestate.

> Note: For solid digestions, the volume reduction stage is critical to obtain accurate data, especially for arsenic. Close monitoring of each sample is necessary when this critical stage is reached.

7.2 Prepare samples for hydride analysis by adding 5.00 g urea, 1.00 g L-cysteine, and 20 mL concentrated HCl to a 25-mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath until the L-cysteine has dissolved and effervescence has subsided (At least 30 minutes is suggested. If effervescense is still seen, repeat step 7.1 with more volume reduction.). Bring flask to volume with reagent water before analyzing. A 1:1 dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard antimony and arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 µg Sb and As/liter.

7.4 If EP extracts (Method 1310) are being analyzed for arsenic, the method of standard additions must be used. Spike appropriate amounts of intermediate or standard antimony and arsenic solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, the borohydride flow around 2.1 mL/min, and the potassium iodide flow around 0.5 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 217.6-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) without background correction if analyzing for antimony. Use the 193.7-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) with background correction for the analysis of arsenic. Begin all flows and allow 10 minutes for warm-up.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder or output meter. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. If a heating coil is not being used, KI must be added to the samples and heated for thirty minutes to ensure reduction.

CAUTION: The hydrides of antimony and arsenic are very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 See section 8.0 of Method 7000.

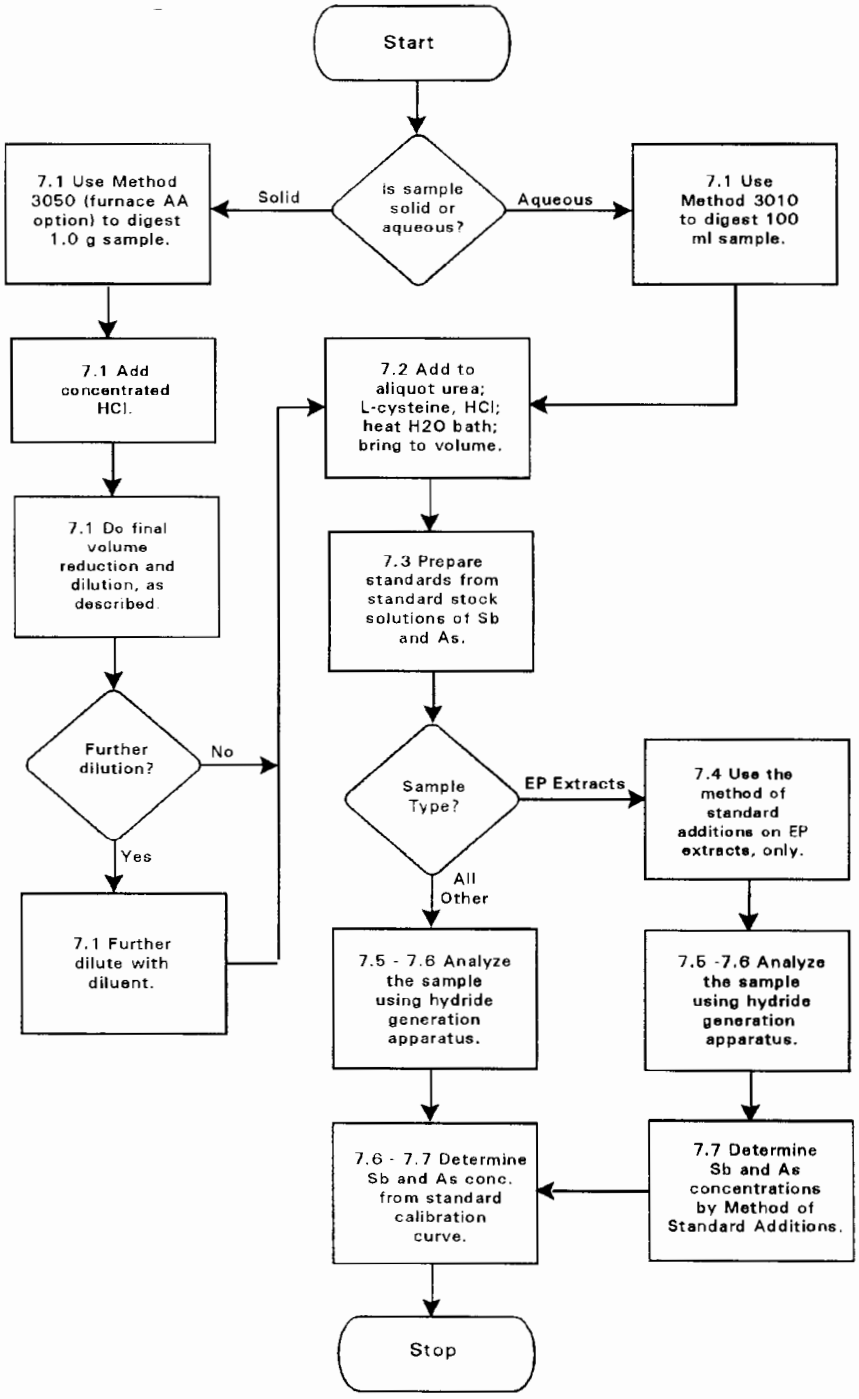
9.0 METHOD PERFORMANCE

9.1 The relative standard deviations obtained by a single laboratory for 7 replicates of a contaminated soil were 18% for antimony at 9.1 ug/L in solution and 4.6% for arsenic at 68 ug/L in solution. The average percent recovery of the analysis of an 8 µg/L spike on ten different samples is 103.7% for arsenic and 95.6% for antimony.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.


Start
is sample solid or aqueous?
Solid
Aqueous
7.1 Use Method 3050 (furnace AA option) to digest 1.0 g sample.
7.1 Use Method 3010 to digest 100 ml sample.
7.1 Add concentrated HCl.
7.2 Add to aliquot urea; L-cysteine, HCl; heat H2O bath; bring to volume.
7.1 Do final volume reduction and dilution, as described.
7.3 Prepare standards from standard stock solutions of Sb and As.
Further dilution?
No
Yes
Sample Type?
EP Extracts
All Other
7.4 Use the method of standard additions on EP extracts, only.
7.1 Further dilute with diluent.
7.5 - 7.6 Analyze the sample using hydride generation apparatus.
7.5 -7.6 Analyze the sample using hydride generation apparatus.
7.6 - 7.7 Determine Sb and As conc. from standard calibration curve.
7.7 Determine Sb and As concentrations by Method of Standard Additions.
Stop

METHOD 7063

ARSENIC IN AQUEOUS SAMPLES AND EXTRACTS
BY ANODIC STRIPPING VOLTAMMETRY (ASV)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for laboratory determinations of free dissolved arsenic in drinking water, natural surface water, seawater, and in domestic and industrial wastewater, and in soil extracts.

1.2 Arsenic concentrations in the linear calibration range of 0.3 to 300 µg/L may be quantified. The upper concentration range may be extended by sample dilution, by decreasing the analyte deposition time, or by increasing the stripping current.

1.3 The method detection limit for free arsenic is about 0.1 µg/L.

1.4 The method is equally sensitive for As(III) and As(V).

2.0 SUMMARY OF METHOD

Standards and samples are made acidic and rendered electrically conductive by adding hydrochloric acid. Free dissolved arsenic is quantified by anodic stripping, at a potential of +145 mV with respect to the saturated calomel electrode (SCE), from a conditioned gold metal film deposited on a glassy carbon electrode (GCE).

3.0 INTERFERENCES

3.1 Dissolved antimony and bismuth are positive interferences. Dissolved copper, at concentrations greater than 1 mg/L, is also a positive interference.

3.2 Turbid samples must be filtered through a borosilicate glass filter with 0.45-µm pores to preclude physical erosion of the GCE gold film.

3.3 Some wet deposition samples may have insufficient electrical conductivity for proper operation of the ASV instrumentation. This problem is obviated by making the solutions 2 M in HCl.

3.4 When the analysis is performed according to the instructions given below, the following ions, compounds, and sample conditions are known not to interfere with the quantitation of arsenic; seawater salts, water-soluble organic compounds such as sugars and tannic acid, and dissolved copper at concentrations less than 100 times the arsenic concentration.

4.0. APPARATUS AND MATERIALS

4.1 ASV instrumentation (Radiometer TraceLab, or equivalent), including potentiostat, electrodes, stirrer, sample stand, polyethylene sample cups, and GCE polishing powder.

4.2 Computer, as recommended by ASV instrumentation manufacturer.

4.3 Plastic syringe and a nylon syringe filter with 0.45-µm pores.

4.4 Adjustable pipetters with polyethylene tips.

4.5 pH meter or pH indicator paper.

4.6 General laboratory glassware, including beakers, graduated cylinders, volumetric flasks, etc.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is interference free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Hydrochloric acid, (concentrated 12 M).

5.3.1 Hydrochloric acid (2 M), dilute 167 mL of concentrated hydrochloric acid to 1 liter with reagent water.

5.3.2 Hydrochloric acid (0.1 M), dilute 50 mL of the 2M hydrochloric acid solution to 1 liter with reagent water.

5.4 Gold Stock Standard (1000 mg/L Au): Stock solutions are commercially available as spectrophotometric standards.

5.4.1 Gold-plating solution, (50 mg/L Au dissolved in 0.1 M HCl): prepare by diluting 2.5 mL of a 1,000 mg/L Au spectrophotometric standard solution to 50 mL with 0.1 M HCl.

5.5 Arsenic Stock Standard (1000 mg/L of arsenic): Stock solutions are commercially available as spectrophotometric standards.

5.5.1 Arsenic intermediate standard solution, 1,000 µg/L arsenic: Dilute 100 µL of the stock standard to 100 mL with 2% HNO_3. Prepare weekly.

5.5.2 Arsenic Working Standards: These standards should be prepared from the arsenic intermediate standard to be used as calibration standards at the time of analysis. Prepare at least five working standards over the linear calibration range of 0.3 µg/L to 300 µg/L by diluting appropriate aliquots of the intermediate arsenic stock solution with 2% HNO_3. The actual concentration of the working standards should cover the anticipated range of sample concentrations.

6.0 SAMPLE HANDLING, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 At the time of sampling, the sample must be acidified to a pH <2 with nitric acid.

6.4 While samples to be analyzed for free dissolved arsenic do not require refrigeration, they should be stored out of direct sunlight in an area no warmer than room temperature.

7.0 PROCEDURE

7.1 Analysis of an aqueous sample for free dissolved arsenic by ASV involves three major steps. First, the GCE electrode must be prepared for use by plating on a thin film of gold; the gold working electrode is then conditioned, and finally, the concentration of free arsenic in the samples are determined.

7.2 Set up ASV instrumentation, electrodes, and computer according to the manufacturer's recommended procedures. Enter the appropriate program and required data parameters into the computer as directed by the instrument software.

7.3 Before applying a gold film to the GCE, the electrode must be thoroughly cleaned. Electrode cleanliness is checked by rinsing the GCE with water. After gently shaking off excess water, the entire electrode should be coated with a thin, flat, unbroken water film. If necessary, clean the GCE by wiping it with a wet, soft paper towel, polishing it with polishing powder, and rinsing it thoroughly with water. Keep the cleaned electrode immersed in water or in air saturated with water vapor.

> Note: Depending on the composition of the samples, a single application of the gold film may suffice for analysis of up to a dozen or more samples. Highly corrosive and oxidizing samples may corrode the gold film and degrade the instrument response, requiring the re-application of the gold film.

7.4 Place 50 mL of the gold-plating solution (Sec. 5.4.1) or an appropriate volume as recommended by the instrument manufacturer, into a beaker. Immerse the electrodes in the gold-plating solution and initiate the GCE gold-plating program as instructed by the instrument manufacturer.

7.5 Following deposition of GCE gold film, the electrode must be conditioned prior to actual sample analysis. Unconditioned electrodes may produce irreproducible arsenic peak areas. Condition electrodes by analyzing an arsenic-free 2 M HCl reagent solution (see 5.3.1) or by analyzing a sample adjusted to contain 2 M HCl (to a 25 mL sample, add 5 mL of concentrated HCl, mix well), according to manufacture's recommended procedures.

7.6 When the conditioning procedure is complete, rinse the electrodes with reagent water and store the electrodes in reagent water until ready to analyze the calibration standards or samples.

7.7 Following the instrument manufacturer's recommended calibration procedures, construct a calibration curve by analyzing five working calibration standards (Sec. 5.5.2);

7.7.1 To 25 mL working standard, add 5 mL concentrated HCl, mix.

7.7.2 Immerse the electrodes into the working standard and record instrument response. Rinse the electrodes thoroughly with reagent water between each standard. Construct a calibration curve by recording the instrument response (peak area or peak height) versus the standard concentration.

7.8 Analyze the samples by aliquoting 25 mL of sample into a beaker. Allow the temperature of the sample to equilibrate to room temperature (within the range of 20 °C to 30 °C) if necessary. Add 5 mL of concentrated HCl to the sample and mix. Immerse the electrodes into the sample and record instrument response. Determine sample concentration from the calibration curve.

8.0 QUALITY CONTROL

8.1 Initial Calibration Verification standard (ICV): The ICV contains a known arsenic concentration and is obtained from an independent source. The ICV recovery must be within the range 90% to 110%. If it is not, the source of error must be found and corrected. An acceptable ICV must be analyzed prior to analyzing samples. The ICV also serves as a laboratory control sample.

8.2 Continuing Calibration Verification standard (CCV): After a set of 10 or fewer samples has been analyzed, and after the final sample has been analyzed, a CCV containing a known arsenic concentration must be analyzed. The CCV recovery must be within the range 90% to 110%. If it is not, the source of error must be found and corrected (see the note in Sec. 7.9) All samples analyzed since the last acceptable CCV must be re-analyzed.

8.3 The analyst must monitor performance of the electrode by analyzing a mid-range check standard every ten samples. A low recovery for the check standard indicates that the electrode must be renewed. Follow the procedures in Sec. 7.3 through 7.5 to renew the gold film on the GCE. Following the renewal of the electrode, the instrument calibration must be verified by analyzing a mid-range standard. If the recovery of the standard is within 10% of the true value, a new calibration curve need not be run.

8.4 Reagent blank: A reagent blank must be analyzed with each analytical batch or 20 samples, whichever is more frequent. A reagent blank is reagent water treated as a sample. The indicated concentration of the reagent blank must not be more than 0.1 µg/L of arsenic. If more than 0.1 µg/L of arsenic is detected in the blank, sample carryover or reagent contamination is indicated. The problem must be corrected before analyzing more samples.

8.5 At least one matrix spike (MS) and one matrix spike duplicate (MSD) shall be included in each analytical batch or 20 samples: A matrix duplicate may be substituted for the MSD provided that the concentration of arsenic in the sample selected for duplicate analysis is greater than the limit of detection. The spike should increase the concentration of free arsenic in the spiked sample by 50% to 200%. The volume of the spike must be no more than 1% of the sample volume.

8.5.1 The spike recovery should within the range 75% to 125%. If the recovery of the spike is outside ± 25%, the problem should be investigated and probable cause determined. If a matrix interference is suspected, a second sample aliquot should be spiked to confirm the spike recovery. If the spike recovery is still outside the range of ± 25%, then that sample and any sample of similar make-up should be quantified by the method of standard additions provided that the results are within 10% of the action level of interest. Refer to Method 7000 for information on the method of standard additions.

8.5.2 The duplicate samples (MS/MSD and/or Sample/Sample duplicate) must give results having a difference not greater than 20% of the mean of the duplicate results. If the difference is greater than 20% of the mean, the source of error must be found and corrected.

9.0 METHOD PERFORMANCE

9.1 In a single-laboratory evaluation, standards with known arsenic concentrations were analyzed according to the instructions given above. The results are listed in Tables 1 and 2.

9.2 In a single-laboratory evaluation, known amounts of arsenic were added to environmental water samples and soil extracts. The results are listed in Table 3.

9.3 In a single-laboratory evaluation, known amounts of arsenic were added to environmental water samples and soil extracts. The resulting solutions were analyzed according to the instruction given above and by graphite furnace atomic absorption spectrophotometry (GFAA). The results are listed in Table 4.

10.0 REFERENCES

1. Pyle, Steven; Miller, Eric Leroy; Quantifying Arsenic In Aqueous Solutions By Anodic Stripping Voltametry, EMSL-LV/ORD/USEPA.

TABLE 1
ACCURACY AND PRECISION OF ARSENIC (III) DETERMINATIONS

Arsenic (III) Concentration (µg/L)	Arsenic (III) Recovery (%)	Relative Standard Deviation (%)
0.700	102	14
7.00	98	2
70.0	100	5

TABLE 2
ACCURACY AND PRECISION OF ARSENIC (V) DETERMINATIONS

Arsenic (V) Concentration (µg/L)	Arsenic (V) Recovery (%)	Relative Standard Deviation (%)
0.700	99	10
7.00	100	1
70.0	99	2

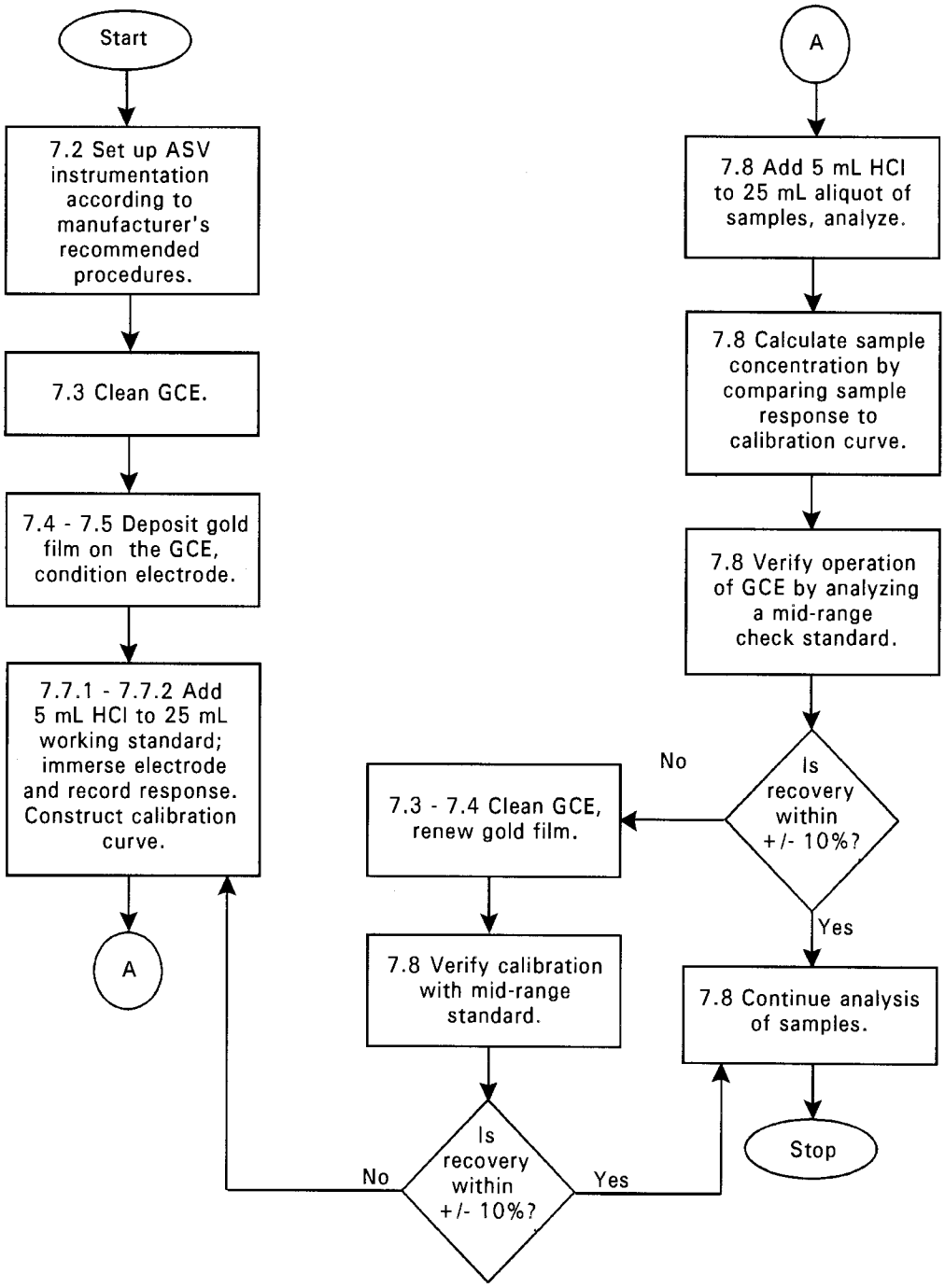
TABLE 3
QUANTIFYING ARSENIC IN ENVIRONMENTAL SAMPLES BY ASV

Sample Identification	Arsenic Added (µg/L)	Arsenic Found (µg/L)	Recovery (%)
Tap Water	20.0	Not Detected	0
Tap Water + 1 g/L Ascorbic Acid	20.0	20.2	101
A12544 (Water	10.0	9.3	93
A12545 (Water)	5.00	5.11	102
A12582 (Water)	10.0	10.0	100
A12582 (Water)	20.0	19.8	99
A24228 (Water)	10.0	10.6	106
A24228 (Water)	20.0	20.5	103
A22949 (Water)	10.0	9.9	99
A22949 (Water)	20.0	20.2	101
A22949 (Water)	50.0	48.2	96
A23274 (Soil Extract)	10.0	12.3	101
A23274 (Soil Extract)	20.0	22.1	99
A23275 (Soil Extract)	10.0	10.5	105
A23275 (Soil Extract)	30.0	31.6	105

TABLE 4
COMPARISON OF ASV AND GFAA RESULTS
FOR ARSENIC IN ENVIRONMENTAL SAMPLES

Sample Identification	Arsenic Added (µg/L)	Arsenic Found, ASV (µg/L)	Arsenic Found, GFAA (µg/L)
A12545 (Water)	5.00	5.11	5.08
A12582 (Water)	10.0	10.0	9.91
A22949 (Water)	50.0	48.2	54.0
A23274 (Soil Extract)	10.0	12.3	12.9
A23275 (Soil Extract)	30.0	31.6	31.5

METHOD 7063
ARSENIC IN AQUEOUS SAMPLES AND EXTRACTS
BY ANODIC STRIPPING VOLTAMMETRY (ASV)



METHOD 7080A

BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High hollow cathode current settings and a narrow spectral band pass must be used, because both barium and calcium emit strongly at barium's analytical wavelength.

3.3 Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. All samples and standards must contain a ionization suppressant. The type of suppressant and concentration used must be documented.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Barium hollow cathode lamp.
4.2.2 Wavelength: 553.6 nm.
4.2.3 Fuel: Acetylene.
4.2.4 Oxidant: Nitrous oxide.
4.2.5 Type of flame: Fuel rich.
4.2.6 Background correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$) analytical reagent grade in reagent water and dilute to 1 liter (1000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards

should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. All calibration standards and samples should contain the ionization suppressant.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Section 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

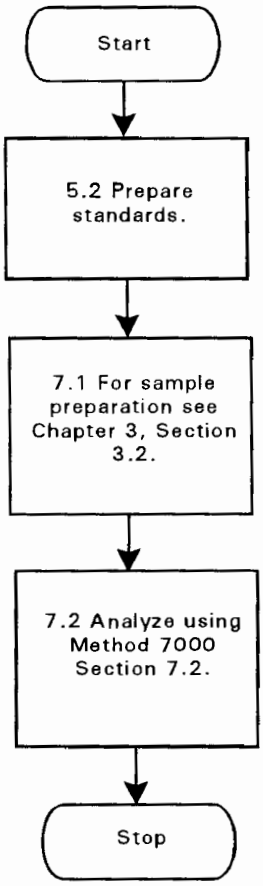
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 553.6 nm.
Sensitivity: 0.4 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.4 and 2 mg Ba/L gave standard deviations of $\pm$0.043 and $\pm$0.13, respectively. Recoveries at these levels were 94% and 113%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 208.1.


Start
5.2 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000 Section 7.2.
Stop

METHOD 7081

BARIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Barium is known to form a barium carbide in the graphite furnace. This less volatile carbide can cause losses of sensitivity and memory effects.

3.3 The long residence time and the high concentration of the analyte in the optical path of the graphite furnace can lead to severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.4 Because of possible chemical interaction, nitrogen should not be used as a purge gas.

3.5 Halide acids should not be used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 1200°C.

4.2.3 Atomizing time and temp: 10 sec at 2800°C.

4.2.4 Purge gas: Argon (nitrogen should not be used).

4.2.5 Wavelength: 553.6 nm.

4.2.6 Background correction: Not required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.7787 g barium chloride ($BaCl_2$ $2H_2O$, analytical reagent grade) in water and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY ASSURANCE

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.


Start
5.0 Prepare standards
7.1 For sample preparation see Chapter 3, Section 3.2
7.2 Analyze using Method 7000 Section 7.3
Stop

METHOD 7090

BERYLLIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction may be required because nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.3 Concentrations of aluminum greater than 500 ppm may suppress beryllium absorbance. The addition of 0.1% fluoride has been found effective in eliminating this interference. High concentrations of magnesium and silicon cause similar problems and require the use of the method of standard additions.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Beryllium hollow cathode lamp.**
4.2.2 **Wavelength:** 234.9 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in Type II water containing 2 mL nitric acid and dilute to 1 liter.

Beryllium metal can also be dissolved in H_2SO_4. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

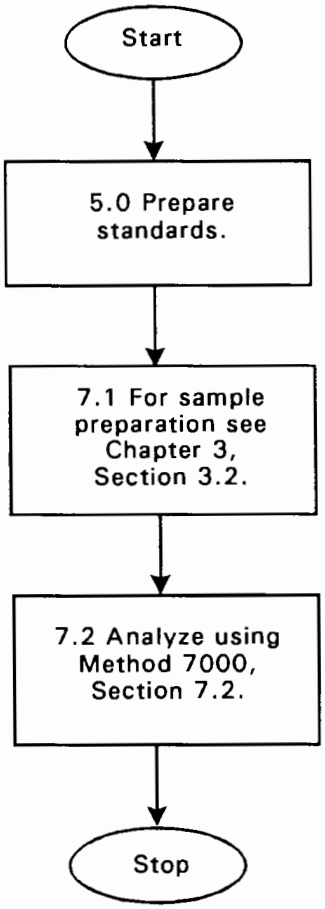
Optimum concentration range: 0.05-2 mg/L with a wavelength of 234.9 nm.
Sensitivity: 0.025 mg/L.
Detection limit: 0.005 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.01 and 0.25 mg/L gave standard deviations of $\pm$0.001 and $\pm$0.002, respectively. Recoveries at these levels were 100% and 97%, respectively.

9.3 For concentrations of beryllium below 0.02 mg/L, the furnace procedure (Method 7091) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 210.1.


Start
5.0 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000, Section 7.2.
Stop

BERYLLIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, beryllium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1000°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2800°C.
4.2.4 **Purge gas:** Argon.
4.2.5 **Wavelength:** 234.9 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in Type II water containing 2 mL concentrated nitric acid and dilute to 1 liter. Beryllium metal can also be dissolved in acid. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

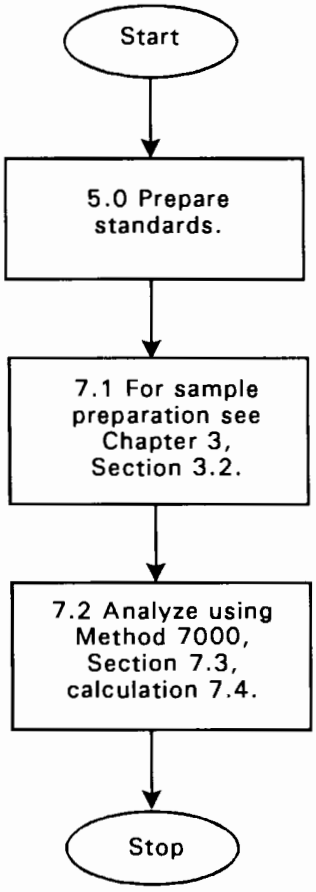
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-30 ug/L.
Detection limit: 0.2 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 210.2.


Start
5.0 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000, Section 7.3, calculation 7.4.
Stop

METHOD 7130

CADMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Nonspecific absorption and light scattering can be significant at the analytical wavelength. Thus background correction is required.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Cadmium hollow cathode lamp.**
4.2.2 **Wavelength:** 228.8 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same

concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.05-2 mg/L with a wavelength of 228.8 nm.
Sensitivity: 0.025 mg/L.
Detection limit: 0.005 mg/L.

9.2 For concentrations of cadmium below 0.02 mg/L, the furnace procedure (Method 7131) is recommended.

9.3 Precision and accuracy data are available in Method 213.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

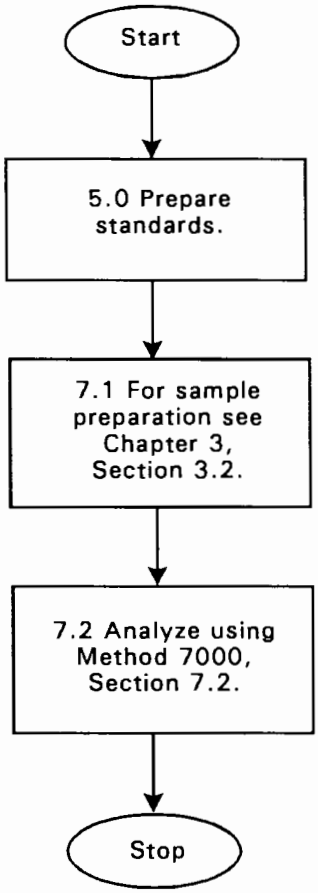
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	2,770, 1,590 ug/g
Wastewater treatment sludge	3050	12,000, 13,000 ug/g


Start
5.0 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000, Section 7.2.
Stop

METHOD 7131A

CADMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, cadmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results.

3.3 Excess chloride may cause premature volatilization of cadmium. Ammonium phosphate used as a matrix modifier minimizes this loss. Other modifiers may be used as long as it is documented with the type of suppressant and concentration.

3.4 Many plastic pipet tips (yellow) contain cadmium. Use "cadmium-free" tips.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 500°C.

4.2.3 Atomizing time and temp: 10 sec at 1900°C.

4.2.4 Purge gas: Argon.

4.2.5 Wavelength: 228.8 nm.

4.2.6 Background correction: Required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.000 g of cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with reagent water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

5.2.3 Ammonium phosphate solution (40%): Dissolve 40 g of ammonium phosphate, $(NH_4)_2HPO_4$ (analytical reagent grade), in reagent water and dilute to 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are provided in Chapter Three, Section 3.2.

7.2 See Method 7000, Section 7.3, Furnace Procedure. The calculation is provided in Method 7000, Section 7.4.

8.0 QUALITY CONTROL

8.1 Refer to Section 8.0 of Method 7000 .

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 213.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 ug/L.
Detection limit: 0.1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

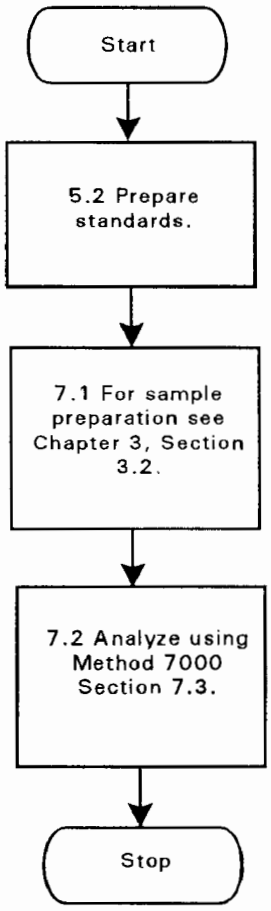
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Lagoon soil	3050	0.10, 0.095 ug/g
NBS SRM 1646 Estuarine sediment	3050	0.35 ug/g[a]
Solvent extract of oily waste	3030	1.39, 1.09 ug/L

[a]Bias of -3% from expected value.


Start
5.2 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000 Section 7.3.
Stop

METHOD 7140

CALCIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 All elements forming stable oxyanions (P, B, Si, Cr, S, V, Ti, Al, etc.) will complex calcium and interfere unless lanthanum is added. Addition of lanthanum to prepared samples rarely presents a problem because virtually all environmental samples contain sufficient calcium to require dilution to be in the linear range of the method.

3.3 PO_4, SO_4, and Al are interferents. High concentrations of Mg, Na, and K interfere.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Calcium hollow cathode lamp.**
4.2.2 **Wavelength:** 422.7 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Stoichiometric.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Suspend 2.500 g of $CaCO_3$ (analytical reagent grade, dried for 1 hr at 180°C) in Type II water and dissolve by adding a minimum of dilute HCl. Dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing, including 1 mL of lanthanum chloride per 10 mL sample or standard (see Paragraph 5.2.3).

5.2.3 **Lanthanum chloride solution:** Dissolve 29 g La_2O_3 in 250 mL concentrated HCl -
CAUTION: REACTION IS VIOLENT -
and dilute to 500 mL with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

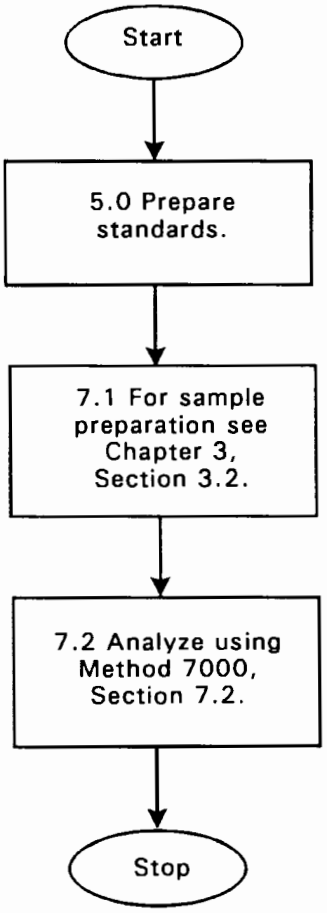
9.1 Precision and accuracy data are available in Method 215.1 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.2-7 mg/L with a wavelength of 422.7 nm.
Sensitivity: 0.08 mg/L.
Detection limit: 0.01 mg/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 215.1.


Start
5.0 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000, Section 7.2.
Stop

CHROMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 An ionization interference may occur if the samples have a significantly higher alkali metal content than the standards. If this interference is encountered, an ionization suppressant (KCl) should be added to both samples and standards.

3.3 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult the specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Chromium hollow cathode lamp.**
4.2.2 **Wavelength:** 357.9 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.923 g of chromium trioxide (CrO_3, analytical reagent grade) in Type II water, acidify with redistilled HNO_3, and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 mg/L with a wavelength of 357.9 nm.
Sensitivity: 0.25 mg/L.
Detection limit: 0.05 mg/L.

9.2 For concentrations of chromium below 0.2 mg/L, the furnace procedure (Method 7191) is recommended.

9.3 Precision and accuracy data are available in Method 218.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

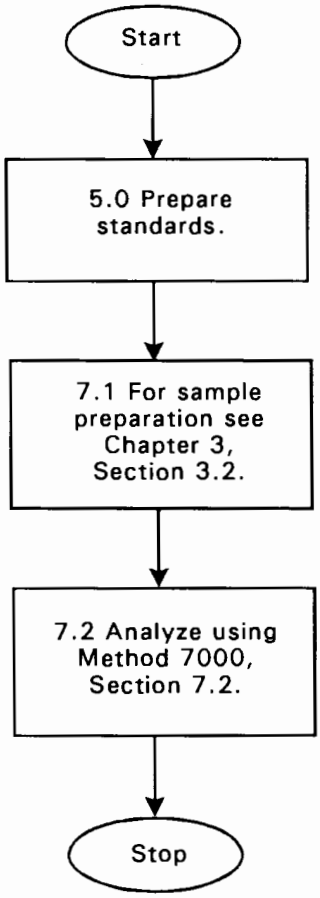
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	6,100, 6,000 ug/g
Emission control dust	3050	2.0, 2.8 ug/g


Start
5.0 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000, Section 7.2.
Stop

CHROMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Low concentrations of calcium and/or phosphate may cause interferences; at concentrations above 200 mg/L, calcium's effect is constant and eliminates the effect of phosphate. Calcium nitrate is therefore added to ensure a known constant effect.

3.3 Nitrogen should not be used as the purge gas because of a possible CN band interference.

3.4 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult the specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1000°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2700°C.
4.2.4 **Purge gas:** Argon (nitrogen should not be used).
4.2.5 **Wavelength:** 357.9 nm.
4.2.6 **Background correction:** Not required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection,

continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.923 g of chromium trioxide (CrO_3, analytical reagent grade) in Type II water, acidify with redistilled HNO_3, and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These standards should be prepared to contain 0.5% (v/v) HNO_3; 1 mL of 30% H_2O_2 and 1 mL of calcium nitrate solution, Section 5.2.3, may be added to lessen interferences (see Section 3.0).

5.2.3 **Calcium nitrate solution:** Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

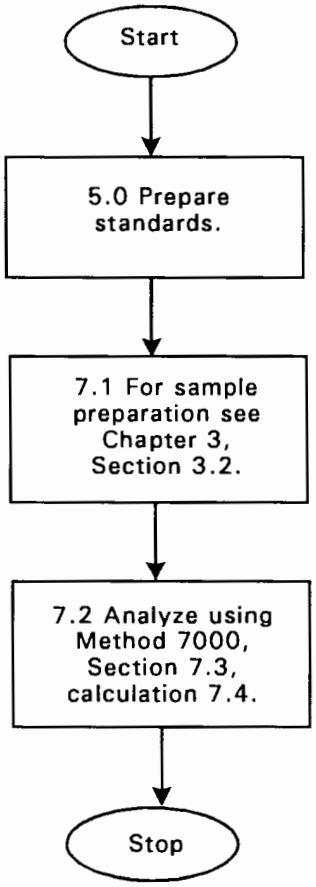
TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Paint primer	3050	2.7, 2.8 mg/g
Contaminated soil	3050	12.0, 12.3 ug/g
Oily lagoon soil	3050	69.6, 70.3 ug/g
NBS SRM 1646 Estuarine sediment	3050	42, 47 ug/g[a]
EPA QC Sludge	3050	156 ug/g[b]
NBS SRM 1085, Wear Metals in lubricating oil	3050	311, 356 ug/g[c]

[a]Bias of -45 and -38% from expected, respectively.

[b]Bias of -24% from expected.

[c]Bias of +4 and +19% from expected, respectively.


Start
5.0 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000, Section 7.3, calculation 7.4.
Stop

METHOD 7195

CHROMIUM, HEXAVALENT (COPRECIPITATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7195 is to be used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7195 may be used to analyze samples containing more than 5 ug of Cr(VI) per liter. Either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191) can be used with coprecipitation.

2.0 SUMMARY OF METHOD

2.1 Method 7195 is based on the separation of Cr(VI) from solution by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate [containing Cr(III)] is drawn off and the precipitate is washed to remove occluded Cr(III). The Cr(VI) is then reduced and resolubilized in nitric acid and quantified as Cr(III) by either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191).

3.0 INTERFERENCES

3.1 Extracts containing either sulfate or chloride in concentrations above 1,000 mg/L should be diluted prior to analysis.

4.0 APPARATUS AND MATERIALS

4.1 Filtering flask: Heavy wall, 1-liter capacity.

4.2 Centrifuge tubes: Heavy duty, conical, graduated, glass-stoppered, 10-mL capacity.

4.3 Pasteur pipets: Borosilicate glass, 6.8 cm.

4.4 Centrifuge: Any centrifuge capable of reaching 2,000 rpm and accepting the centrifuge tubes described in Section 4.2 may be used.

4.5 pH meter: A wide variety of instruments are commercially available and suitable for this work.

4.6 Test tube mixer: Any mixer capable of imparting a thorough vortex is acceptable.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Lead nitrate solution: Dissolve 33.1 g of lead nitrate, $Pb(NO_3)2$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.3 Ammonium sulfate solution: Dissolve 2.7 g of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.4 Calcium nitrate solution: Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 100 mL (1 mL = 20 mg Ca).

5.5 Nitric acid: Concentrated, distilled reagent grade or spectrograde quality.

5.6 Acetic acid, glacial, 10% (v/v): Dilute 10 mL glacial acetic acid, CH_3COOH (ACS reagent grade), to 100 mL with Type II water.

5.7 Ammonium hydroxide, 10% (v/v): Dilute 10 mL concentrated ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with Type II water.

5.8 Hydrogen peroxide, 30%: ACS reagent grade.

5.9 Potassium dichromate standard solution: Dissolve 28.285 g of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in Type II water and dilute to 1 liter (1 mL = 10 mg Cr).

5.10 Trivalent chromium working stock solution: To 50 mL of the potassium dichromate standard solution, add 1 mL of 30% H_2O_2 and 1 mL concentrated HNO_3 and dilute to 100 mL with Type II water (1 mL = 5.0 mg trivalent chromium). Prepare fresh monthly, or as needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis is 24 hr.

7.0 PROCEDURE

7.1 Transfer a 50-mL portion of the sample to a 100-mL Griffin beaker and adjust to a pH of 3.5 $\pm$ 0.3 by adding volumes of 10% acetic acid dropwise. Proceed immediately to Step 7.2, taking no longer than 15 min between these steps.

NOTE: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to <3, 10% NH_4OH should be used to readjust the pH to 3.5 $\pm$ 0.3.

7.2 Pipet a 10-mL aliquot of the adjusted sample into a centrifuge tube. Add 100 uL of the lead nitrate solution, stopper the tube, mix the sample, and allow to stand for 3 min.

7.3 After the formation of lead chromate, to help retain Cr(III) complex in solution, add 0.5 mL glacial acetic acid, stopper, and mix.

7.4 To provide adequate lead sulfate for coprecipitation, add 100 uL of ammonium sulfate solution, stopper, and mix.

7.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2,000 rpm in small increments over a period of 5 min. Hold at 2,000 rpm for 1 min.

NOTE: The speed of the centrifuge must be increased slowly to ensure complete coprecipitation.

7.6 After centrifuging, remove the tube and withdraw and discard the supernate using either the apparatus detailed in Figure 1 or careful decantation. If using the vacuum apparatus, the pasteur pipet is lowered into the tube and the supernate is sucked over into the filtering flask. With care, the supernate can be withdrawn to within approximately 0.1 mL above the precipitate. Wash the precipitate with 5 mL Type II water and repeat steps 7.5 and 7.6; then proceed to 7.7.

7.7 To the remaining precipitate, add 0.5 mL concentrated HNO_3, 100 uL 30% H_2O_2, and 100 uL calcium nitrate solution. Stopper the tube and mix, using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10 mL, mix, and analyze in the same manner as the calibration standard.

7.8 Flame atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 1 to 10 mg Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7090 for more detail.

7.9 Furnace atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 5 to 100 ug Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7191 for more detail.

7.10 Verification:

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting precipitation. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be less than 30 ug/L Cr(VI). To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed. If necessary, use furnace atomic absorption to achieve the optimal concentration range.

7.10.4 If the interference persists after sample dilution, an alternative method (Method 7197, Chelation/Extraction, or Method 7196, Colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

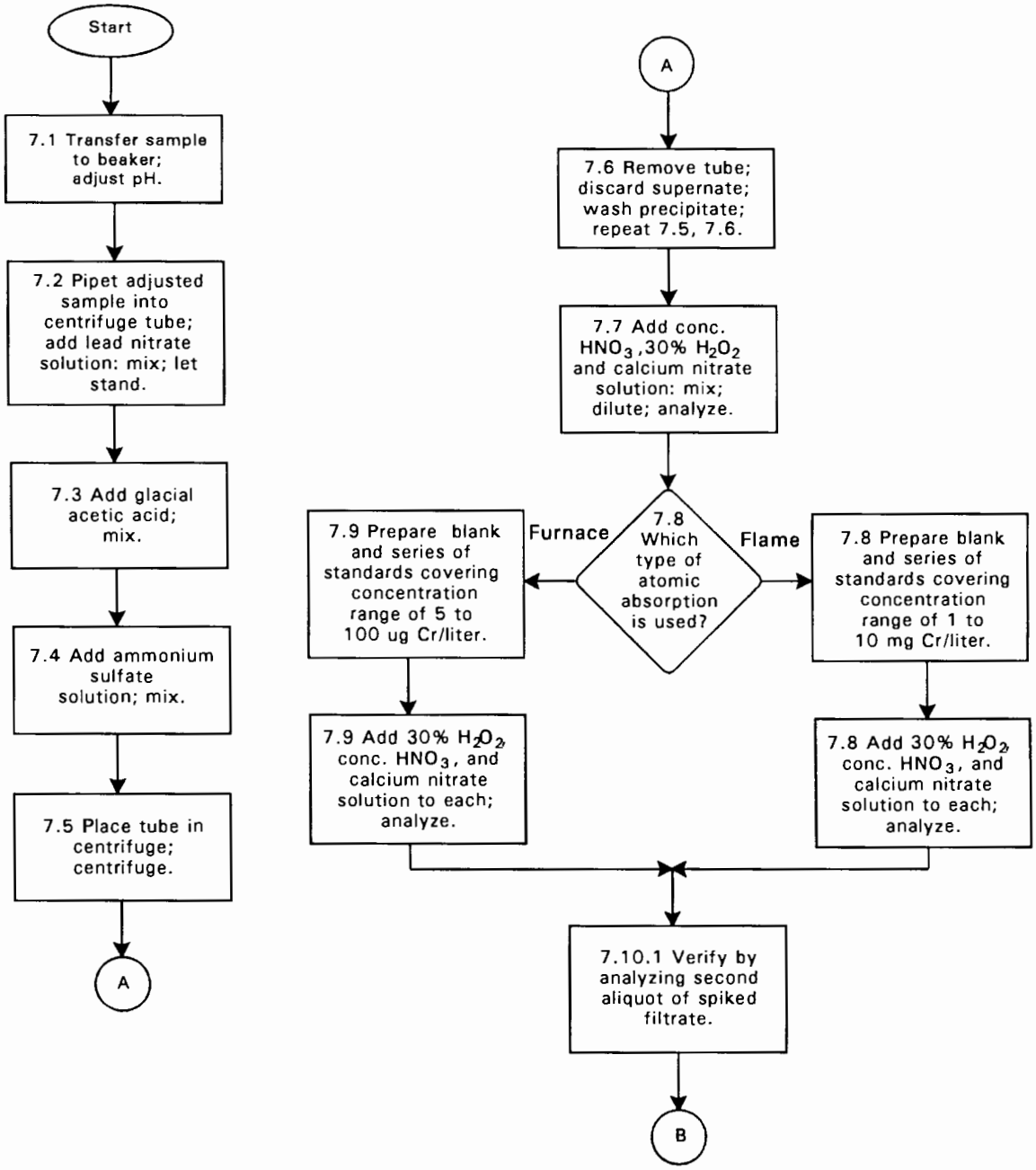
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

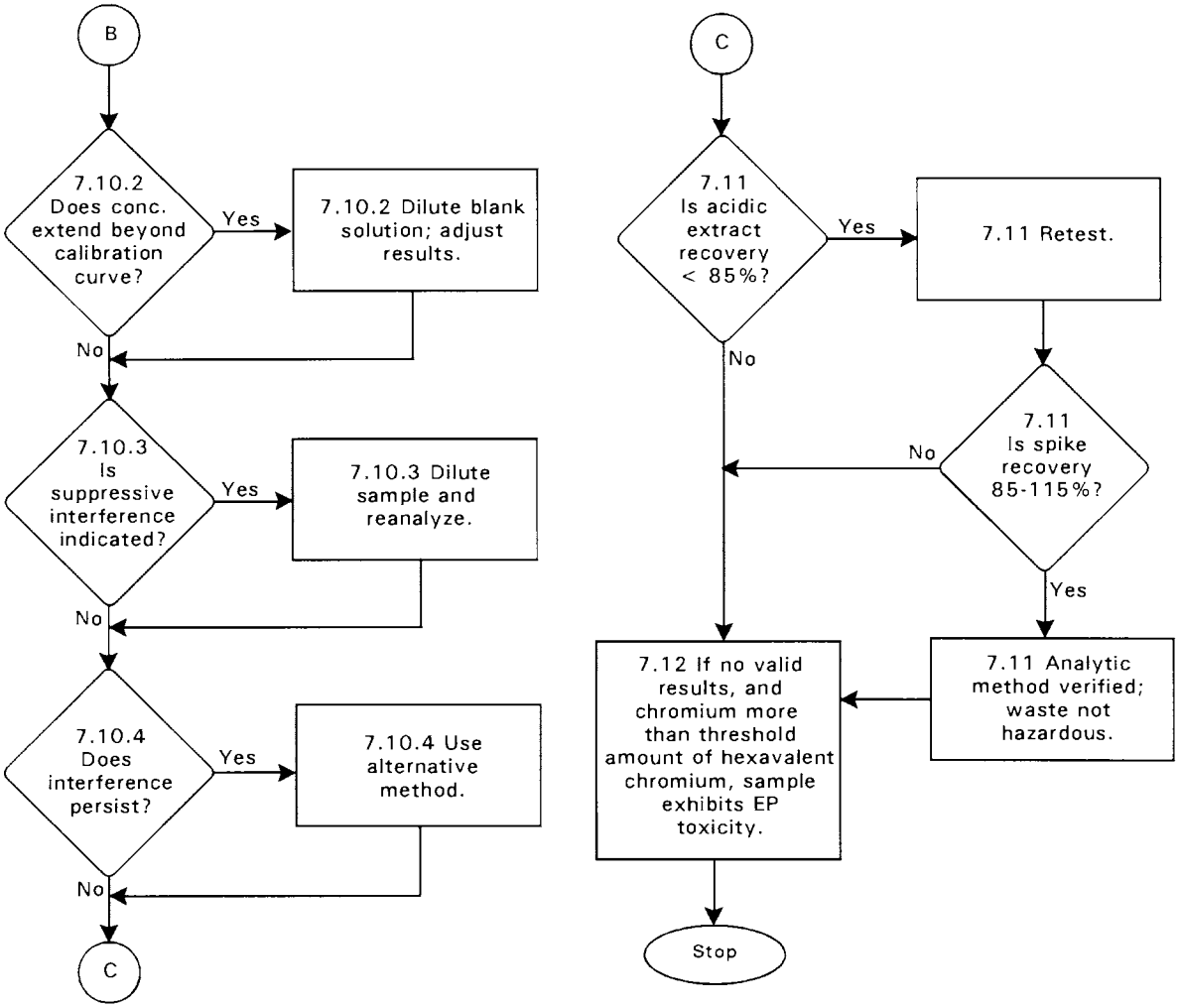
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.5 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.5.


Start
7.1 Transfer sample to beaker; adjust pH.
7.2 Pipet adjusted sample into centrifuge tube; add lead nitrate solution: mix; let stand.
7.3 Add glacial acetic acid; mix.
7.4 Add ammonium sulfate solution; mix.
7.5 Place tube in centrifuge; centrifuge.
A
A
7.6 Remove tube; discard supernate; wash precipitate; repeat 7.5, 7.6.
7.7 Add conc. HNO_3, 30% H_2O_2 and calcium nitrate solution: mix; dilute; analyze.
7.8 Which type of atomic absorption is used?
Furnace
Flame
7.9 Prepare blank and series of standards covering concentration range of 5 to 100 ug Cr/liter.
7.8 Prepare blank and series of standards covering concentration range of 1 to 10 mg Cr/liter.
7.9 Add 30% H_2O_2, conc. HNO_3, and calcium nitrate solution to each; analyze.
7.8 Add 30% H_2O_2, conc. HNO_3, and calcium nitrate solution to each; analyze.
7.10.1 Verify by analyzing second aliquot of spiked filtrate.
B


B
7.10.2 Does conc. extend beyond calibration curve?
Yes
7.10.2 Dilute blank solution; adjust results.
No
7.10.3 Is suppressive interference indicated?
Yes
7.10.3 Dilute sample and reanalyze.
No
7.10.4 Does interference persist?
Yes
7.10.4 Use alternative method.
No
C
C
7.11 Is acidic extract recovery < 85%?
Yes
7.11 Retest.
No
7.11 Is spike recovery 85-115%?
No
Yes
7.11 Analytic method verified; waste not hazardous.
7.12 If no valid results, and chromium more than threshold amount of hexavalent chromium, sample exhibits EP toxicity.
Stop

METHOD 7196A

CHROMIUM, HEXAVALENT (COLORIMETRIC)

1.0 SCOPE AND APPLICATION

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in EP/TCLP characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 INTERFERENCES

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

4.0 APPARATUS AND MATERIALS

4.1 Colorimetric equipment: One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

5.0 REAGENTS

5.1 Reagent water: Reagent water should be monitored for impurities.

5.2 Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in reagent water and dilute to 1 liter (1 mL = 50 ug Cr).

5.3 Potassium dichromate standard solution: Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 5 ug Cr).

5.4 Sulfuric acid, 10% (v/v): Dilute 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, H_2SO_4, to 100 mL with reagent water.

5.5 Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.6 Acetone (analytical reagent grade): Avoid or redistill material that comes in containers with metal or metal-lined caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis of the samples or extracts is 24 hr. The 24 hr holding time begins after extraction.

7.0 PROCEDURE

7.1 Color development and measurement: Transfer 95 mL of the extract to be tested to a 100-mL volumetric flask. Add 2.0 mL diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 $\pm$ 0.5, dilute to 100 mL with reagent water, and let stand 5 to 10 min for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use reagent water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method (see Note below). An aliquot of the sample containing all reagents except diphenylcarbazide should be prepared and used to correct the sample for turbidity (i.e., a turbidity blank). From the corrected absorbance, determine the mg/L of chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in Step 7.1, above, take an absorbance reading before adding the carbazide

reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

7.2 Preparation of calibration curve:

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet a chromium standard solution in measured volumes into 250-mL beakers or conical flasks to generate standard concentrations ranging from 0.5 to 5 mg/L Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell and measure the absorbance at 540 nm. As reference, use reagent water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/L of Cr(VI).

7.3 Verification:

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 µg Cr(VI)/liter. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7197, Chelation/Extraction) should be used.

7.4 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

7.5 Analyze all extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for more information.

8.2 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.3 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one matrix spike replicate or one replicate sample for every ten samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Refer to Chapter One for more information concerning matrix spikes and matrix spike duplicates.

8.6 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

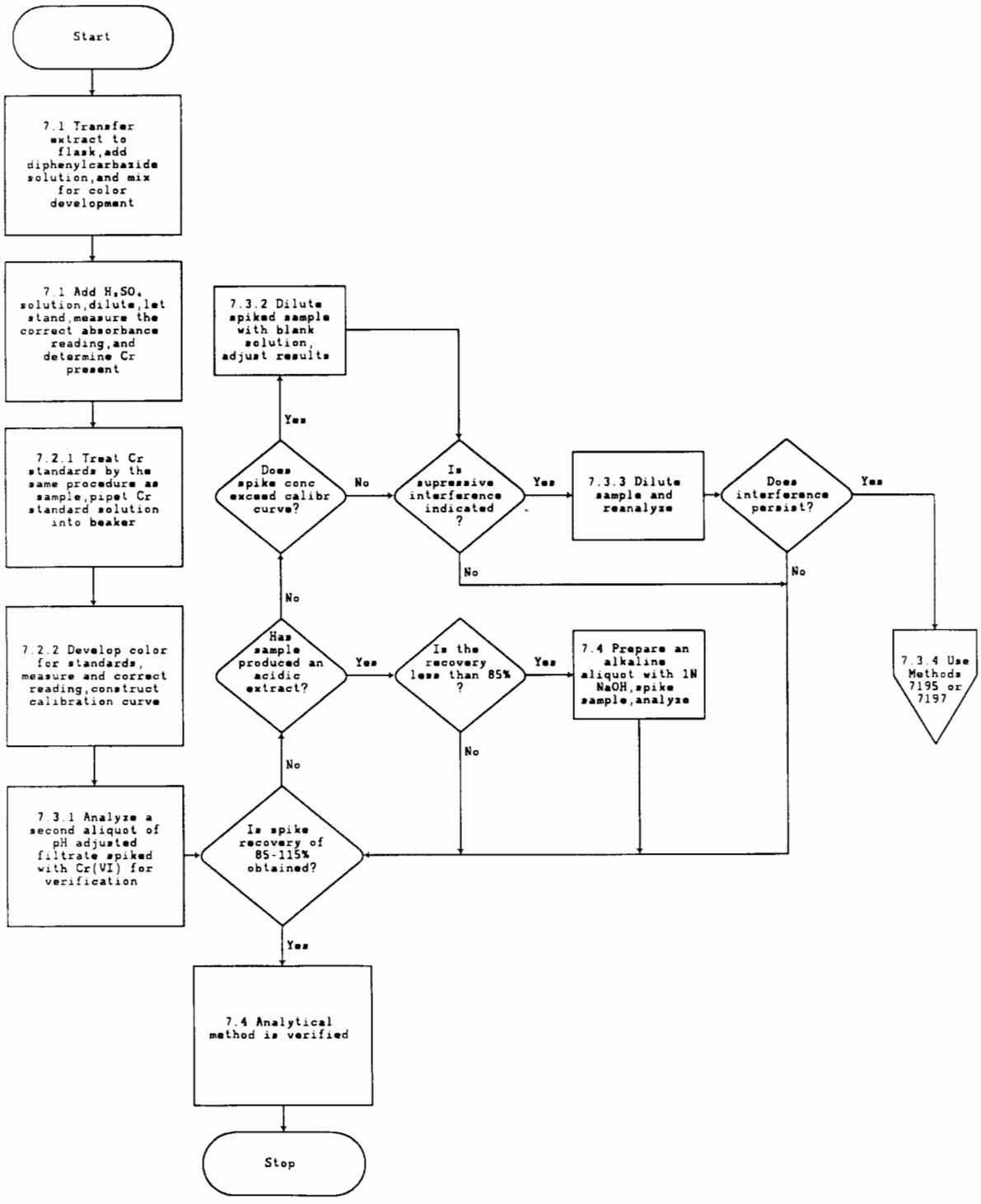
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Methods 218.4 and 218.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	Not known	0.096, 0.107 ug/g
Sediment from chemical storage area	3060	115, 117 ug/g


Start
7.1 Transfer extract to flask, add diphenylcarbazide solution, and mix for color development
7.1 Add H2SO4 solution, dilute, let stand, measure the correct absorbance reading, and determine Cr present
7.2.1 Treat Cr standards by the same procedure as sample, pipet Cr standard solution into beaker
7.2.2 Develop color for standards, measure and correct reading, construct calibration curve
7.3.1 Analyze a second aliquot of pH adjusted filtrate spiked with Cr(VI) for verification
Is spike recovery of 85-115% obtained?
No
Yes
7.4 Analytical method is verified
Stop
7.3.2 Dilute spiked sample with blank solution, adjust results
Does spike conc exceed calibr curve?
No
Yes
Is supressive interference indicated ?
Yes
No
7.3.3 Dilute sample and reanalyze
Does interference persist?
Yes
No
7.3.4 Use Methods 7195 or 7197
Has sample produced an acidic extract?
No
Yes
Is the recovery less than 85% ?
Yes
No
7.4 Prepare an alkaline aliquot with 1N NaOH, spike sample, analyze

Revision 1

METHOD 7197

CHROMIUM, HEXAVALENT (CHELATION/EXTRACTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7197 is approved for determining the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1).

1.2 Method 7197 may be used to analyze samples containing from 1.0 to 25 ug of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Method 7197 is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of an atomic absorption spectrophotometer.

3.0 INTERFERENCES

3.1 High concentrations of other metals may interfere.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Chromium hollow cathode lamp.

4.3 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Ammonium pyrrolidine dithiocarbamate (APDC) solution: Dissolve 1.0 g APDC in Type II water and dilute to 100 mL. Prepare fresh daily.

5.3 Bromphenol blue indicator solution: Dissolve 0.1 g bromphenol blue in 100 mL 50% ethanol.

5.4 Potassium dichromate standard solution I (1.0 mL = 100 ug Cr): Dissolve 0.2829 g pure dried potassium dichromate, $K_2Cr_2O_7$, in Type II water and dilute to 1,000 mL.

5.5 Potassium dichromate standard solution II (1.0 mL = 10.0 ug Cr): Dilute 100 mL chromium standard solution I to 1 liter with Type II water.

5.6 Potassium dichromate standard solution III (1.0 mL = 0.10 ug Cr): Dilute 10.0 mL chromium standard solution II to 1 liter with Type II water.

5.7 Methyl isobutyl ketone (MIBK), analytical reagent grade: Avoid or redistill material that comes in contact with metal or metal-lined caps.

5.8 Sodium hydroxide solution, 1 M: Dissolve to 40 g sodium hydroxide, NaOH (ASC reagent grade), in Type II water and dilute to 1 liter.

5.9 Sulfuric acid, 0.12 M: Slowly add 6.5 mL distilled reagent grade or spectrograde-quality sulfuric acid, H_2SO_4, to Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Because the stability of Cr(VI) in EP extracts is not completely understood at this time, the chelation and extraction should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed.

7.0 PROCEDURE

7.1 Pipet a volume of extract containing less than 2.5 ug chromium (100 mL maximum) into a 200-mL volumetric flask and adjust the volume to approximately 100 mL.

7.2 Prepare a blank and sufficient standards and adjust the volume of each to approximately 100 mL.

7.3 Add 2 drops of bromphenol blue indicator solution. (The adjustment of pH to 2.4, Step 7.4, may be made with a pH meter instead of using an indicator.)

7.4 Adjust the pH by addition of 1 M NaOH solution dropwise until a blue color persists. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears in both the standards and sample. Then add 2.0 mL of 0.12 M H_2SO_4 in excess. The pH at this point should be 2.4.

7.5 Add 5.0 mL APDC solution and mix. The pH should then be approximately 2.8.

7.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

7.7 Allow the layers to separate and add Type II water until the ketone layer is completely in the neck of the flask.

7.8 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

7.9 Determine the mg/liter of Cr(VI) in each sample from a plot of scale readings of standards. A working curve must be prepared with each set of samples.

7.10 Verification:

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting chelation. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 ug/L Cr(VI). To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.10.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7196, Colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

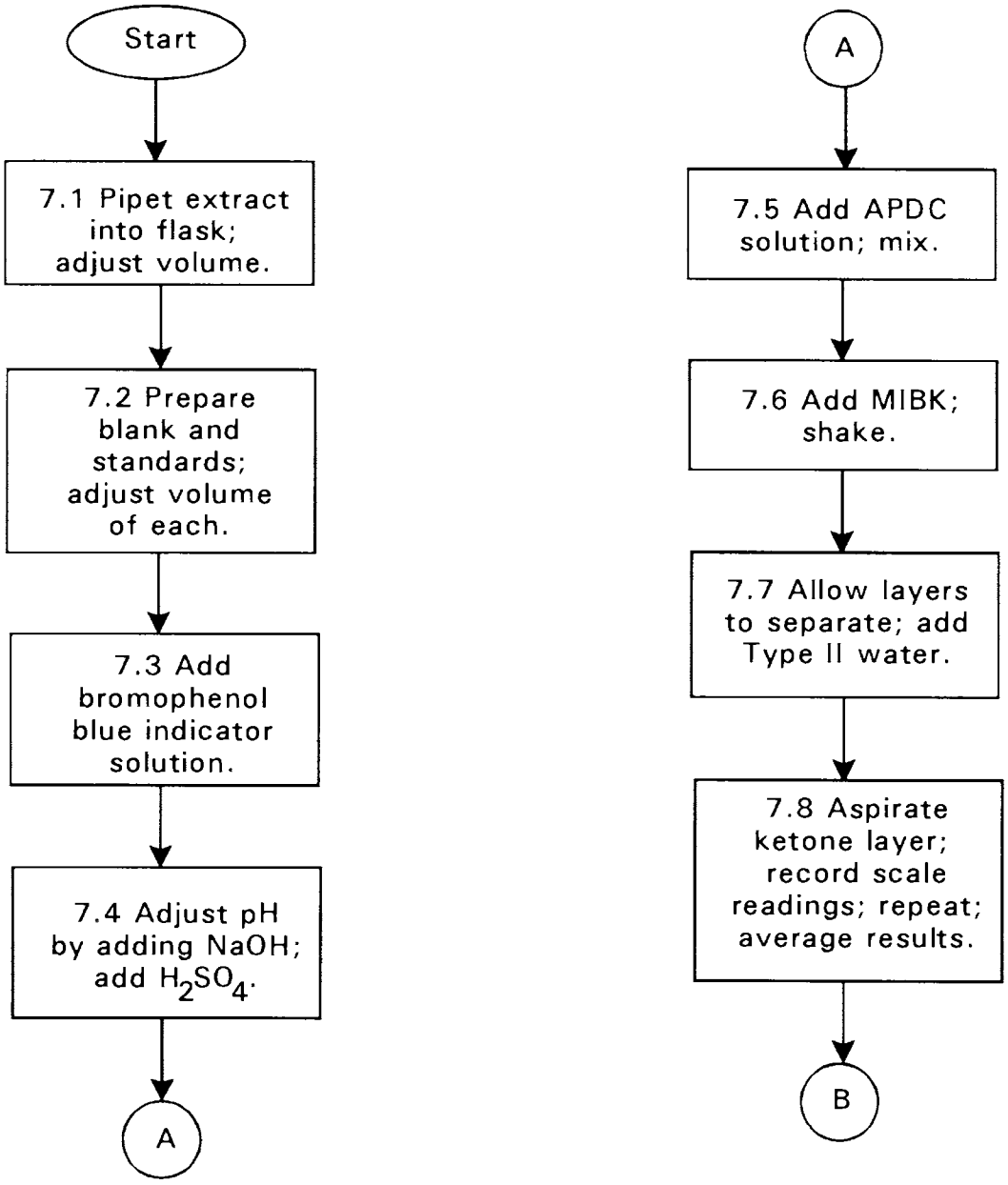
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

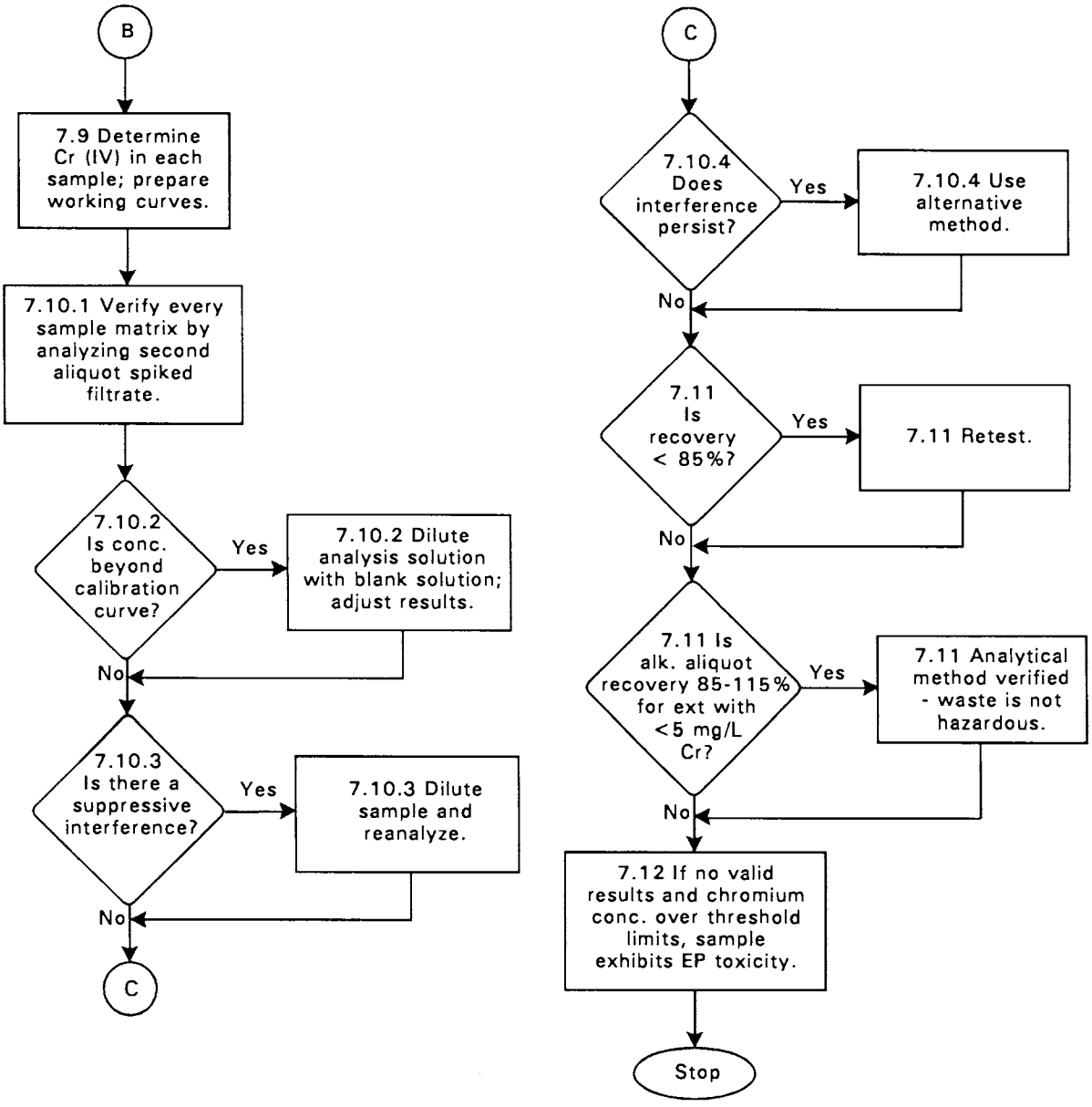
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.4 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.4.


Start
7.1 Pipet extract into flask; adjust volume.
7.2 Prepare blank and standards; adjust volume of each.
7.3 Add bromophenol blue indicator solution.
7.4 Adjust pH by adding NaOH; add H_2SO_4.
A
A
7.5 Add APDC solution; mix.
7.6 Add MIBK; shake.
7.7 Allow layers to separate; add Type II water.
7.8 Aspirate ketone layer; record scale readings; repeat; average results.
B


B
7.9 Determine Cr (IV) in each sample; prepare working curves.
7.10.1 Verify every sample matrix by analyzing second aliquot spiked filtrate.
7.10.2 Is conc. beyond calibration curve?
Yes
7.10.2 Dilute analysis solution with blank solution; adjust results.
No
7.10.3 Is there a suppressive interference?
Yes
7.10.3 Dilute sample and reanalyze.
No
C
C
7.10.4 Does interference persist?
Yes
7.10.4 Use alternative method.
No
7.11 Is recovery < 85%?
Yes
7.11 Retest.
No
7.11 Is alk. aliquot recovery 85-115% for ext with <5 mg/L Cr?
Yes
7.11 Analytical method verified - waste is not hazardous.
No
7.12 If no valid results and chromium conc. over threshold limits, sample exhibits EP toxicity.
Stop

CHROMIUM, HEXAVALENT (DIFFERENTIAL PULSE POLAROGRAPHY)

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of hexavalent chromium [Cr(VI)] in natural and waste waters and in EP extracts.

1.2 The method can quantitate chromium in concentrations of up to 1.0 mg/L to 5.0 mg/L, depending on the mercury drop size. Higher concentrations can be determined by dilution.

1.3 The lower limit of detection for Cr(VI) is 10 ug/L for the instrumental conditions given in this method. The limit of detection could be easily lowered by changing these conditions.

2.0 SUMMARY OF METHOD

2.1 Method 7198 measures the peak current produced from the reduction of Cr(VI) to Cr(III) at a dropping mercury electrode during a differential pulse voltage ramp.

2.2 The method described herein uses 0.125 M NH_4OH-0.125 M NH_4Cl as the supporting electrolyte. In this electrolyte, Cr(VI) reduction results in peak current occurring at the peak potential (Ep) of -0.250 V vs. Ag/AgCl.

2.3 Alternative supporting electrolytes, such as those given in Table 1, may be used.

2.4 The technique of standard additions must be used to quantitate the Cr(VI) content.

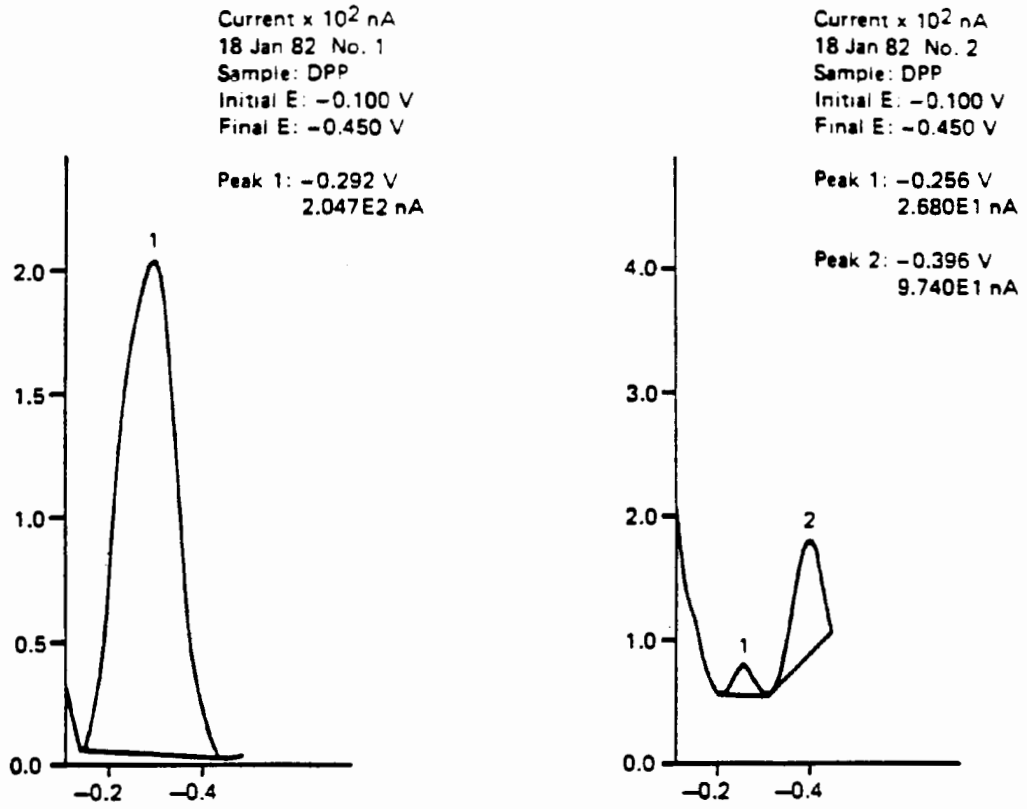
3.0 INTERFERENCES

3.1 Copper ion at concentrations higher than the Cr(VI) concentration is a potential interference due to peak overlap when using the 0.125 M ammoniacal electrolyte. Increasing the ammoniacal electrolyte concentration to 0.5 M shifts the copper peak cathodically (Ep = -0.4 V), eliminating the interference at a copper-to-chromium ratio of 10:1 (Figure 1).

3.2 Reductants such as ferrous iron, sulfite, and sulfide will reduce Cr(VI) to Cr(III); thus it is imperative to analyze the samples as soon as possible.

4.0 APPARATUS AND MATERIALS

4.1 Polarographic instrumentation: Capable of performing differential pulse analyses, including recorder or plotter.



A. 20 ppm Cu, 2.5 ppm Cr, 0.1 N buffer.

B. 20 ppm Cu, 2.5 ppm Cr, 0.5 N buffer.

Figure 1. Two polarograms illustrating shift in copper peak at higher ammoniacal electrolyte concentrations.

TABLE 1. POLAROGRAPHY OF HEXAVALENT CHROMIUM

Supporting electrolyte	Peak potential (vs. SCE)
1 M NaOH	-0.85
1 M Pyridine, 1 M NaOH	-1.48
1 M NH_4OH, 1 M NH_4Cl	-0.36
0.1 M NH_4OH, 0.1 M $(NH_4)_2$ Tartrate	-0.244
0.2 M KCl, 0.3 M Triethanolamine, pH 9	-0.28
1 M Na_2SO_4	-0.23
0.1 M NH_4OH, 0.1 M NH_4Cl	-0.25

4.2 Dropping mercury electrode assembly: Capable of performing differential pulse analyses.

4.3 Counter electrode: Platinum wire.

4.4 Reference electrode: Ag/AgCl or SCE, with a slow-leakage fritted tip (unfired Vycor).

4.5 Nitrogen gas and cell outgassing assembly.

4.6 Micropipets and disposable tips.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Chromium standard solution I, 1.0 mL = 100 ug Cr: Should be made daily from a 1,000-ppm standard stock solution made with Type II water.

5.3 Chromium standard solution II, 1.0 mL = 10 ug Cr: Should be made daily from a 1,000-ppm standard stock solution made with Type II water.

5.4 Chromium standard solution III, 1.0 mL = 1 ug Cr: Dilute 10 mL chromium standard solution II to 100 mL with Type II water.

5.5 Ammoniacal electrolyte, 2.5 N: Dissolve 33.3 g of NH_4Cl in 150 mL of Type II water, add 42.2 mL of concentrated NH_4OH, and dilute to 250 mL.

5.6 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Stability of Cr(VI) is not completely understood at this time. Therefore, the analysis should be carried out as soon as possible.

6.3 If the analysis cannot be performed within 24 hr, take an aliquot of the sample and add a known amount of Cr(VI) (0.1 mg/L for natural waters, 1 mg/L for wastewaters, and 5 mg/L for EP extracts). Analyze this known additional sample at the same time the sample is analyzed to determine whether Cr(VI) was reduced during storage.

6.4 To retard the chemical activity of Cr(VI), the sample should be transported and stored at 4°C until time of analysis.

7.0 PROCEDURE

7.1 Soak the voltammetric cells overnight in 1 + 1 HNO_3 and/or 1 + 1 aqua regia.

7.2 Rinse the electrode assembly with Type II water, then with 1 N HNO_3, and finally with Type II water prior to and in between sample analyses.

7.3 The instrument should be set using the following instrumental parameters.

7.3.1 **Mode:** Differential pulse.
7.3.2 **Scan rate:** 2 mV/sec.
7.3.3 **Drop time:** 1 sec.
7.3.4 **Initial potential:** -0.05 V $\pm$ 0.05 V vs. Ag/AgCl.
7.3.5 **Final potential:** -0.50 V $\pm$ 0.10 V vs. Ag/AgCl.
7.3.6 **Pulse height:** 0.05 V.
7.3.7 **Deaeration time:** 240 sec or less initially, 30 sec between standard additions.

7.4 Analysis:

7.4.1 Pipet a volume of sample containing less than 10 ug Cr(VI) into a voltammetric cell (the maximum volume depends on the voltammetric cell volume, usually 10 mL).

7.4.2 Add 0.5 mL of the ammoniacal electrolyte and adjust volume to 10 mL with Type II water.

7.4.3 Place the electrode assembly in the solution and outgas with nitrogen for at least 120 sec.

7.4.4 Engage the electrode assembly to the polarographic analyzer and displace at least 10 mercury drops before initiating the voltage ramp and obtaining the polarogram.

7.4.5 Figure 2 gives typical differential pulse polarograms.

7.5 Prior to the analysis of any samples, and during analysis at a frequency of at least once every 10 samples, verify that the cell contamination is less than 10 ug/L Cr by analyzing demineralized water and the appropriate volume of supporting electrolyte in a manner similar to the procedure described in 7.4.3 and 7.4.4.

7.6 Calibration:

7.6.1 After running a differential pulse polarogram on the sample solution, quantitate the chromium using the technique of standard addition.

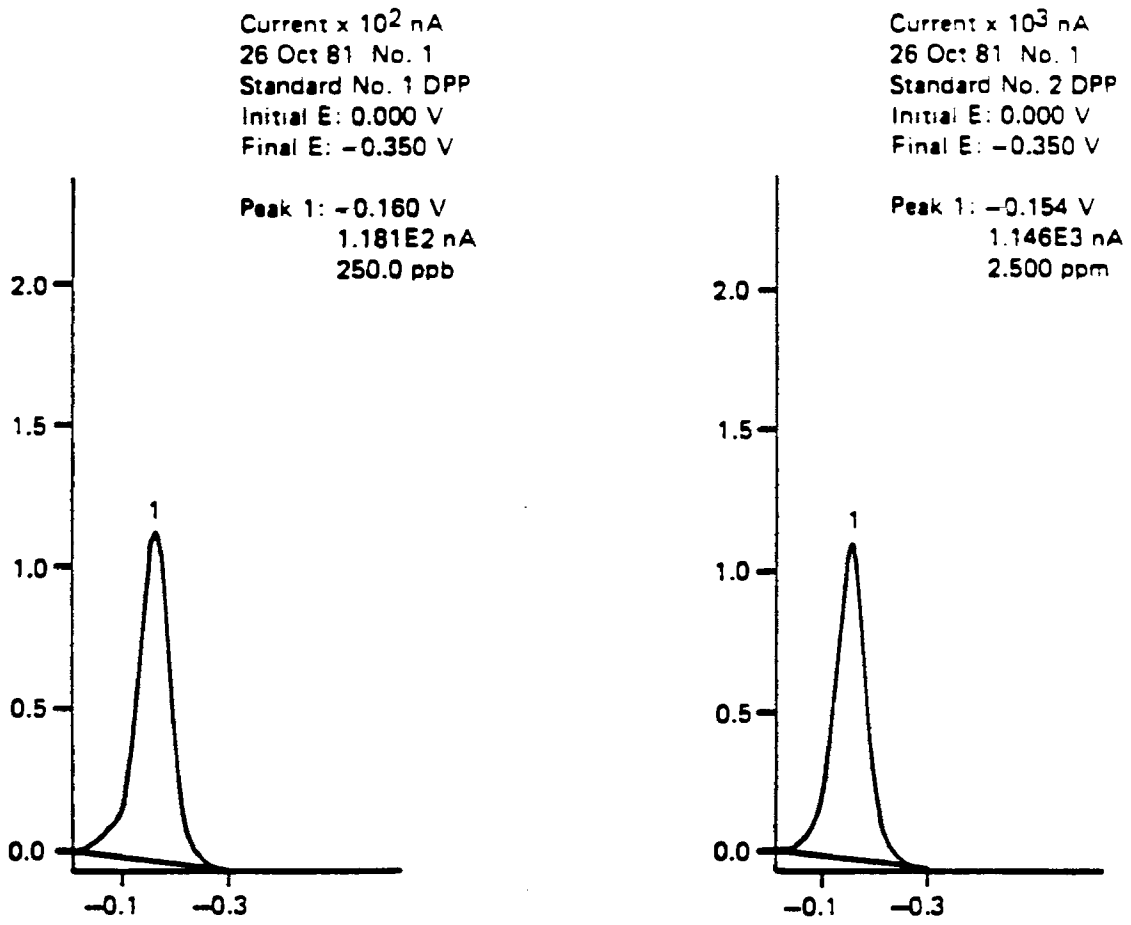


Figure 2. Typical differential pulse polarogram at 0.25 ppm and 2.5 ppm Cr in 0.1 N buffer.

7.6.2 Three standard additions should be made to obtain the best precision and accuracy. The first standard addition should be approximately one-half the concentration of the sample, the second equal to that of the sample, and the third about 1.5 times the sample concentration. The total volume due to standard additions should not exceed the cell value by more than 10%.

7.6.3 Add an appropriate aliquot of chromium standard solution I, II, or III to the sample in the cell. Deaerate for 30 sec to mix the solution and remove oxygen added with the known addition.

7.6.4 Repeat the analysis procedure, beginning with Step 7.4.4 for each standard addition.

7.7 Calculations:

7.7.1 Calculate the concentration of chromium determined by each standard addition procedure as follows:

$$C_u = \frac{i_1 V_i C_s}{i_1 V_i + (i_1 - i_1)V} \times \frac{V}{V_u}$$

where:

i_1 = Current peak height for the sample (nA);

i_i = Current peak height for the sample plus standard (nA);

V_u = Volume of sample in the cell (mL);

V_i = Volume of standard taken for spiking (mL);

V = Volume in cell prior to standard addition;

C_s = Concentration of standard used to spike (mg/L); and

C_u = Concentration of the unknown in the sample (mg/L).

7.7.2 Some microprocessor polarographic systems will perform these calculations automatically.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 If necessary, dilute samples so that they fall within the working range.

8.3 Quantitation must be performed by the method of standard additions (see Method 7000, Section 8.7).

8.4 Verify calibration with an independently prepared check standard every 15 samples (see Chapter One, Section 1.1.8).

8.5 Standards should be compared to a reference standard on a routine basis.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data for this method are summarized in Table 2.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.4 and 218.5.

TABLE 2. PRECISION AND ACCURACY OF THE DPP OF HEXAVALENT CHROMIUM

2a. Precision

Sample type	No. of replicates	Average value	% RSD
Leachate[a]	3	1.87	0.69

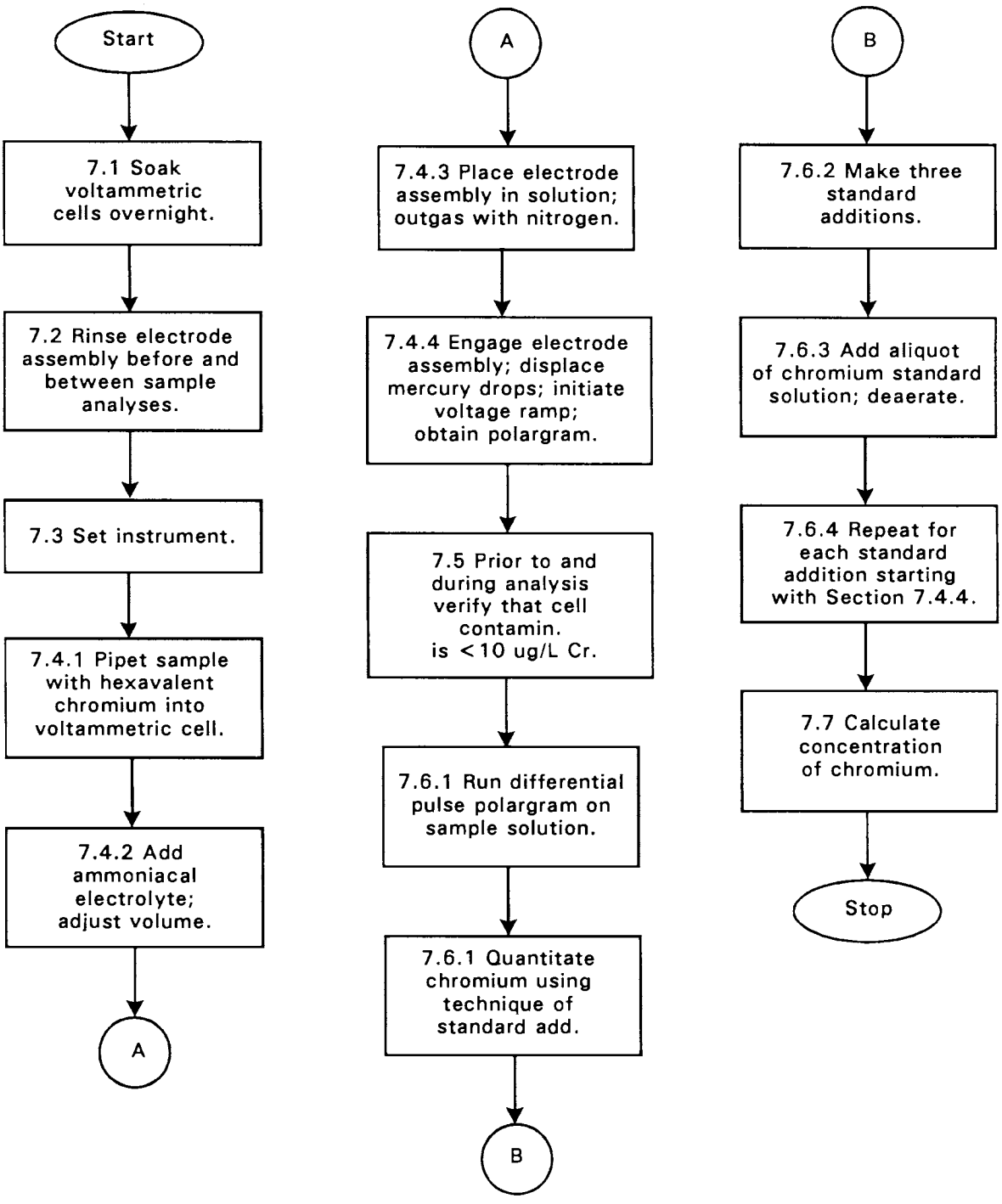
2b. Accuracy (spike recovery data)

Sample type	Spike level (mg/L)	No. of samples	Average % recovery	Standard deviation of % recovery
EP extracts	5.0	8	92.8	6.4

2c. Methods comparison

	Diff. pulse polarography	APDC extraction ICAP-OES	Ion chromatography coupled to ICAP-OES
Value[a]	1.87	1.84	1.91

[a]Leachate sample from a waste disposal site.


Start
7.1 Soak voltammetric cells overnight.
7.2 Rinse electrode assembly before and between sample analyses.
7.3 Set instrument.
7.4.1 Pipet sample with hexavalent chromium into voltammetric cell.
7.4.2 Add ammoniacal electrolyte; adjust volume.
A
A
7.4.3 Place electrode assembly in solution; outgas with nitrogen.
7.4.4 Engage electrode assembly; displace mercury drops; initiate voltage ramp; obtain polargram.
7.5 Prior to and during analysis verify that cell contamin. is <10 ug/L Cr.
7.6.1 Run differential pulse polargram on sample solution.
7.6.1 Quantitate chromium using technique of standard add.
B
B
7.6.2 Make three standard additions.
7.6.3 Add aliquot of chromium standard solution; deaerate.
7.6.4 Repeat for each standard addition starting with Section 7.4.4.
7.7 Calculate concentration of chromium.
Stop

METHOD 7199

DETERMINATION OF HEXAVALENT CHROMIUM IN DRINKING WATER, GROUNDWATER AND INDUSTRIAL WASTEWATER EFFLUENTS BY ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of hexavalent chromium in drinking water, groundwater, and industrial wastewater effluents.

1.2 The method detection limits for the above matrices are listed in Table 1. The MDL obtained by an individual laboratory for a specific matrix may differ from those listed depending on the nature of the sample and the instrumentation used.

1.3 Samples containing high levels of anionic species such as sulfate and chloride may cause column overload. Samples containing high levels of organics or sulfides cause rapid reduction of soluble Cr(VI) to Cr(III). Samples must be stored at 4°C and analyzed within twenty-four hours of collection.

1.4 This method should be used by analysts experienced in the use of ion chromatography and in the interpretation of ion chromatograms.

2.0 SUMMARY OF METHOD

2.1 An aqueous sample is filtered through a 0.45 µm filter and the filtrate is adjusted to a pH of 9 to 9.5 with a buffer solution. A measured volume of the sample (50-250 µL) is introduced into the ion chromatograph. A guard column removes organics from the sample before the Cr(VI) as CrO_4^{2-} is separated on an anion exchange separator column. Post-column derivatization of the Cr(VI) with diphenylcarbazide is followed by detection of the colored complex at 530 nm.

3.0 INTERFERENCES

3.1 Interferences which affect the accurate determination of Cr(VI) may come from several sources.

3.1.1 Contamination - A trace amount of Cr is sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this method to adjust the pH of samples, reagent blanks should be analyzed to assess for potential Cr(VI) contamination. Contamination can also come from improperly cleaned glassware or contact or caustic or acidic reagents of samples with stainless steel or pigmented material.

3.1.2 Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. However, at a pH of 6.5 or greater, CrO_4^{2-} which is less reactive than the $HCrO_4^-$, is the predominant species.

3.1.3 Overloading of the analytical column capacity with high concentrations of anionic species, especially chloride and sulfate, will cause a loss of Cr(VI). The column specified in this method can handle samples containing up to 5% sodium sulfate or 2%

sodium chloride (1). Poor recoveries from fortified samples and tailing peaks are typical manifestations of column overload.

4.0 APPARATUS AND MATERIALS

4.1 Ion Chromatograph.

4.1.1 Instrument equipped with a pump capable of withstanding a minimum backpressure of 2000 psi and of delivering a constant flow in the range of 1-5 mL/min and containing no metal parts in the sample, eluant or reagent flow path.

4.1.2 Helium gas supply (High purity, 99.995%).

4.1.3 Pressurized eluant container, plastic, one or two liter size.

4.1.4 Sample loops of various sizes (50 - 250 µL).

4.1.5 A pressurized reagent delivery module with a mixing tee and beaded mixing coil.

4.1.6 Guard Column - A column placed before the separator column containing a sorbent capable of removing strongly absorbing organics and particles that would otherwise damage the separator column (Dionex IonPac NG1 or equivalent).

4.1.7 Analytical Column - A column packed with a high capacity anion exchange resin capable of resolving CrO_4^{2-} from other sample constituents (Dionex IonPack AS7 or equivalent).

4.1.8 Postcolumn reactor - Mixing tee, or membrane reactor, with reaction coil. Must be compatible with flows from 0 to 2 mL/min.

4.1.9 A low-volume flow-through cell visible lamp detector containing no metal parts in contact with the eluant flow path. Detection wavelength is at 530 nm.

4.1.10 Recorder, integrator, or computer for receiving analog or digital signals for recording detector response (peak height or area) as a function of time.

4.2 Labware - All reusable glassware (glass, quartz, polyethylene, Teflon, etc.) including the sample containers should be soaked overnight in laboratory grade detergent and water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (1+2+9) followed by rinsing with tap water and Reagent water. Alternative cleaning procedures are permitted, provided that adequate cleanliness can be demonstrated through the analysis of method blanks.

NOTE: Chromic acid must not be used for the cleaning of glassware.

4.2.1 Volumetric flasks and a graduated cylinder - of acceptable precision and accuracy.

4.2.2 Assorted calibrated pipettes - of acceptable precision and accuracy.

4.2.3 Disposable syringes - 10-mL, with male luer-lock fittings.

4.2.4 Syringe filters - 0.45-µm.

4.2.5 Storage bottle - high density polypropylene, 1-L capacity.

4.2.6 pH meter - to read pH range 0 - 14 with accuracy ± 0.03 pH.

4.2.7 Filter discs - 0.45-µm pore, 7.3-cm diameter (Gelman Acro 50A, Mfr. No. 4262, or equivalent).

4.2.8 Plastic syringe filtration unit (Baxter Scientific, Cat. No. 1240 IN, or equivalent).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.1.1 Ammonium hydroxide, NH_4OH (sp.gr. 0.902) (CAS RN 1336-21-6).

5.1.2 Ammonium sulfate, $(NH_4)_2\ SO_4$ (CAS RN 7783-20-2).

5.1.3 1,5-Diphenylcarbazide (CAS RN 140-22-7).

5.1.4 Methanol, HPLC grade.

5.1.5 Sulfuric acid, concentrated (sp.gr. 1.84).

5.2 Reagent water. Reagent water shall be interference-free and should conform to the performance specifications of ASTM Type I water. All references to water in the method refer to reagent water unless otherwise specified. A definition of reagent water can be found in Chapter One.

5.3 Cr(VI) Stock Solution (1000 mg/L). Dissolve 4.501 g of $Na_2CrO_4 \cdot 4H_2O$ in reagent water and dilute to one liter. Transfer to a polypropylene storage container.

5.4 Quality control sample (QCS). Obtained and prepared from an independent source (EPA, NIST or from a commercial source). Dilute an aliquot according to the instructions and analyze with samples. If an EPA or NIST reference sample is not available, a mid-range standard, prepared from an independent commercial source, may be used.

5.5 Eluant. Dissolve 33 g of ammonium sulfate in 500 mL of reagent water and add 6.5 mL of ammonium hydroxide. Dilute to one liter with reagent water. Degass the solution with helium gas for 5-10 minutes prior to use.

5.6 Post-column reagent. Dissolve 0.5 g of 1,5 diphenylcarbazide in 100 mL of HPLC grade methanol in a 1000 mL volumetric flask. In a separate container, add 28 mL of 98% sulfuric acid into 500 mL of reagent water, mix, and degass with helium gas for 5-10 minutes prior to adding to the diphenylcarbazide solution. Dilute to volume with reagent water. Reagent is stable for four or five days, but should only be prepared in one liter quantities as needed.

5.7 Buffer Solution. Dissolve 33 g of ammonium sulfate in 75 mL of reagent water and add 6.5 mL of ammonium hydroxide. Dilute to 100 mL with reagent water. Degass the solution with helium gas for 5-10 minutes prior to use.

5.8 Dilution Water. A batch of reagent grade water must be prepared by adjusting the pH within the range of 9-9.5 using the buffer solution. Use this solution for diluting working standards and high level samples.

5.9 Helium Gas.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Prior to the collection of the sample, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration and pH adjustment should be performed at the time of sample collection or as soon thereafter as practically possible.

6.2 For the determination of dissolved Cr(VI), the sample should be filtered through a 0.45-µm filter. Use a portion of the sample to rinse the syringe filtration unit and filter and then collect the required volume of filtrate. Adjust the pH of the sample to 9-9.5 by dropwise addition of buffer solution (Section 5.7), periodically checking the pH with the pH meter or narrow pH-range pH paper. If salts are formed as a result of the pH adjustment, the filtrate must be filtered again prior to analysis. Approximately 10 mL of sample are sufficient for three IC analyses.

6.3 Ship and store the samples at 4°C in 125-mL narrow-mouth, high-density polypropylene containers, or equivalent. Bring to ambient temperature prior to analysis. Samples should be analyzed within 24 hours of collection.

7.0 PROCEDURE

7.1 Sample preparation. Allow pH-adjusted samples to equilibrate to ambient temperature prior to analysis. Samples that have not been pH adjusted should be adjusted as described in Section 6.2.

7.2 Calibration. Calibrate the instrument using a minimum of a calibration blank and three calibration standards bracketing the anticipated concentration range of the samples. The calibration range must cover no more than two orders of magnitude. Calibration standards should be prepared from the Cr(VI) stock standard (Section 5.3) by appropriate dilution using the dilution water (Section 5.8) in volumetric flasks.

7.2.1 Establish ion chromatographic operating conditions as indicated in Table 2 or as instructed by the instrument manufacturer. The flow rate of the eluant pump is set at 1.5 mL/min and the pressure of the reagent delivery module adjusted so that the final flow

rate from the detector is 2.0 mL/min. This requires manual adjustment and measurement of the final flow using a graduated cylinder and a stop watch. A warm-up period of approximately 30 minutes after the flow rate has been adjusted is recommended and the flow rate should be checked prior to calibration and sample analysis.

7.2.2 Injection loop size is chosen based on standard and sample concentrations and the selected attenuator setting. A 250-µL loop was used to establish the method detection limits in Table 1. A 50-µL loop is normally sufficient for higher concentrations. The sample volume used to load the injection loop should be at least 10 times the loop size so that all tubing in contact with sample is thoroughly flushed with new sample to prevent cross contamination.

7.2.3 A calibration curve of analyte response (peak height or area) versus analyte concentration should be constructed. The coefficient of correlation for the curve should be 0.999 or greater.

7.3 Instrument performance. Check the performance of the instrument and verify the calibration using data gathered from analyses of laboratory blanks, calibration standards and the quality control sample.

7.3.1 After the calibration has been established, it must be verified by analyzing a QCS. If the measured concentration exceeds ± 10% of the established value, a second analysis should be performed. If the measured concentration still exceeds ± 10% the established value, the analysis should be terminated until the source of the problem is identified and corrected.

7.3.2 To verify that the instrument is properly calibrated on a continuing basis, run a laboratory blank and a calibration check standard every ten analyses. If the measured concentration of the analyte deviates from the true concentration by more than ± 10%, re-analyze the calibration check standard. If this check standard deviates by more than ± 10%, the instrument must be recalibrated and the previous ten samples re-analyzed. The instrument response from the calibration check may be used for recalibration purposes. Refer to Section 7.2 for instrument calibration procedures.

7.4 Sample Analysis. Draw into a new, unused syringe approximately 3 mL of sample and attach a syringe filter to the syringe. Discard 0.5 mL through the filter and load the remaining sample (equal to at least 10X the sample loop volume) into sample loop. Samples having concentrations higher than the established calibration range must be diluted into the calibration range and re-analyzed. Each sample should be injected twice and the Relative Standard Deviation of the duplicates should be less than 20% or the sample data must be qualified.

7.5 Calculations.

7.5.1 From the calibration curve the concentration of the sample can be determined. For the above procedure, if there is no dilution, the concentration of the sample should be reported as µg/L.

7.5.2 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for the appropriate quality control procedures.

8.2 All quality control data should be maintained and available for easy reference or inspection.

8.3 Calibration curves should be composed of a minimum of a blank and three standards.

8.4 Samples exceeding the highest calibration standard must be diluted and re-analyzed.

8.5 A minimum of one method blank sample per sample batch must be analyzed to check for contamination. A method blank is reagent water prepared by adjusting the pH to between 9 and 9.5 with the same volume of buffer as used for the samples.

8.6 A minimum of one duplicate sample and one matrix spike sample per sample batch must be analyzed for each analytical batch to check for duplicate precision and matrix-spike recovery.

8.7 A quality control sample (QCS) must be analyzed at the beginning of each analytical run to validate the instrument calibration.

9.0 METHOD PERFORMANCE

9.1 Instrument operating conditions used for single laboratory testing of the method are summarized in Table 2. Dissolved Cr(VI) method detection limits are listed in Table 1.

9.2 Data obtained from single laboratory testing of the method are summarized in Table 3 for five water samples representing drinking water, deionized water, groundwater, treated municipal sewage wastewater, and treated electroplating wastewater. Samples were fortified with 100 and 1000 µg/L of Cr(VI), and recoveries were determined.

9.3 Pooled Precision and Accuracy: This method was tested by 21 volunteer laboratories in a joint study by USEPA and the American Society for Testing and Materials (ASTM). Mean recovery and accuracy for Cr(VI) (as CrO_4^{2-}) was determined from the retained data of 13 laboratories in reagent water, drinking water, groundwater, and various industrial wastewaters. For reagent water, the mean recovery and the overall and single-analyst relative standard deviations were 105%, 7.8%, and 3.9%, respectively. Table 4 contains the linear equations that describe the single-analyst standard deviation and mean recovery of Cr(VI) in reagent water.

10.0 REFERENCES

1. Dionex Technical Note No. 26, May 1990.

2. Glaser, J.A., Foerst, D.L., McKee, G.D., Quave, S.A., and Budde, W.L., "Trace Analyses for Wastewaters", Environmental Science and Technology, Vol. 15, No. 12, 1981, pp. 1426-1435.

3. Edgell, K., Longbottom, J., and Joyce, R., "Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography: Collaborative Study", (Internal EPA report, 1992).

4. Arar, Elizabeth J., and Pfaff, John D., "Determination of Dissolved Hexavalent Chromium in Industrial Wastewater Effluents by Ion Chromatography and Post-Column Derivatization with Diphenylcarbazide", Journal of Chromatography, 546 (1991) 335-340.

TABLE 1
METHOD DETECTION LIMIT FOR Cr(VI)

Matrix Type	Retention Time (min)	Method Detection Limit[(a)] µg/L
Reagent Water	3.8	0.4
Drinking Water	3.8	0.3
Ground Water	3.8	0.3
Primary Sewage Wastewater	3.8	0.3
Electroplating Wastewater	3.8	0.3

[(a)] MDL concentrations are computed for final analysis solution (Section 8.2.2)

TABLE 2
ION CHROMATOGRAPHIC CONDITIONS

Columns:	Guard Column - Dionex Ionpac NGI Separator Column - Dionex IonPac AS7
Eluant:	250 mM $(NH_4)_2SO_4$ 100 mM NH_4 Flow Rate = 1.5 mL/min
Post-Column Reagent:	2mM Diphenylcarbohydrazide 10% v/v CH_3OH 1 N H_2SO_4 Flow rate = 0.5 mL/min
Detector:	Visible 530 nm

TABLE 3
SINGLE-LABORATORY PRECISION AND ACCURACY

Sample Type	Cr(VI) (µg/L)[a]	Percent Mean Recovery	RPD[b]
Reagent Water	100	100	0.8
	1000	100	0.0
Drinking Water	100	105	6.7
	1000	98	1.5
Ground Water	100	98	0.0
	1000	96	0.8
Primary Sewage	100	100	0.7
Wastewater	1000	104	2.7
Electroplating	100	99	0.4
Wastewater	1000	101	0.4

[a] Sample spiked at this concentration level.
[b] RPD - relative percent difference between duplicates.

TABLE 4
SINGLE-ANALYST PRECISION, OVERALL PRECISION AND RECOVERY
FROM MULTILABORATORY STUDY

	Reagent Water (6-960 µg/L)	Matrix Water (6-960 µg/L)
Mean Recovery	X = 1.020C + 0.592	X = 0.989C - 0.411
Overall Standard Deviation	S_R= 0.035X + 0.893	S_R= 0.059X + 1.055
Single-Analyst Standard-Deviation	S_R= 0.021X + 0.375	S_R= 0.041X + 0.393

X = Mean concentration; µg/L, exclusive of outliers.
C = True value, µg/L.
S_R= Overall standard deviation.
S_R= Single-Analyst standard deviation.

DETERMINATION OF HEXAVALENT CHROMIUM IN DRINKING WATER, GROUNDWATER AND INDUSTRIAL WASTEWATER EFFLUENTS BY ION CHROMATOGRAPHY

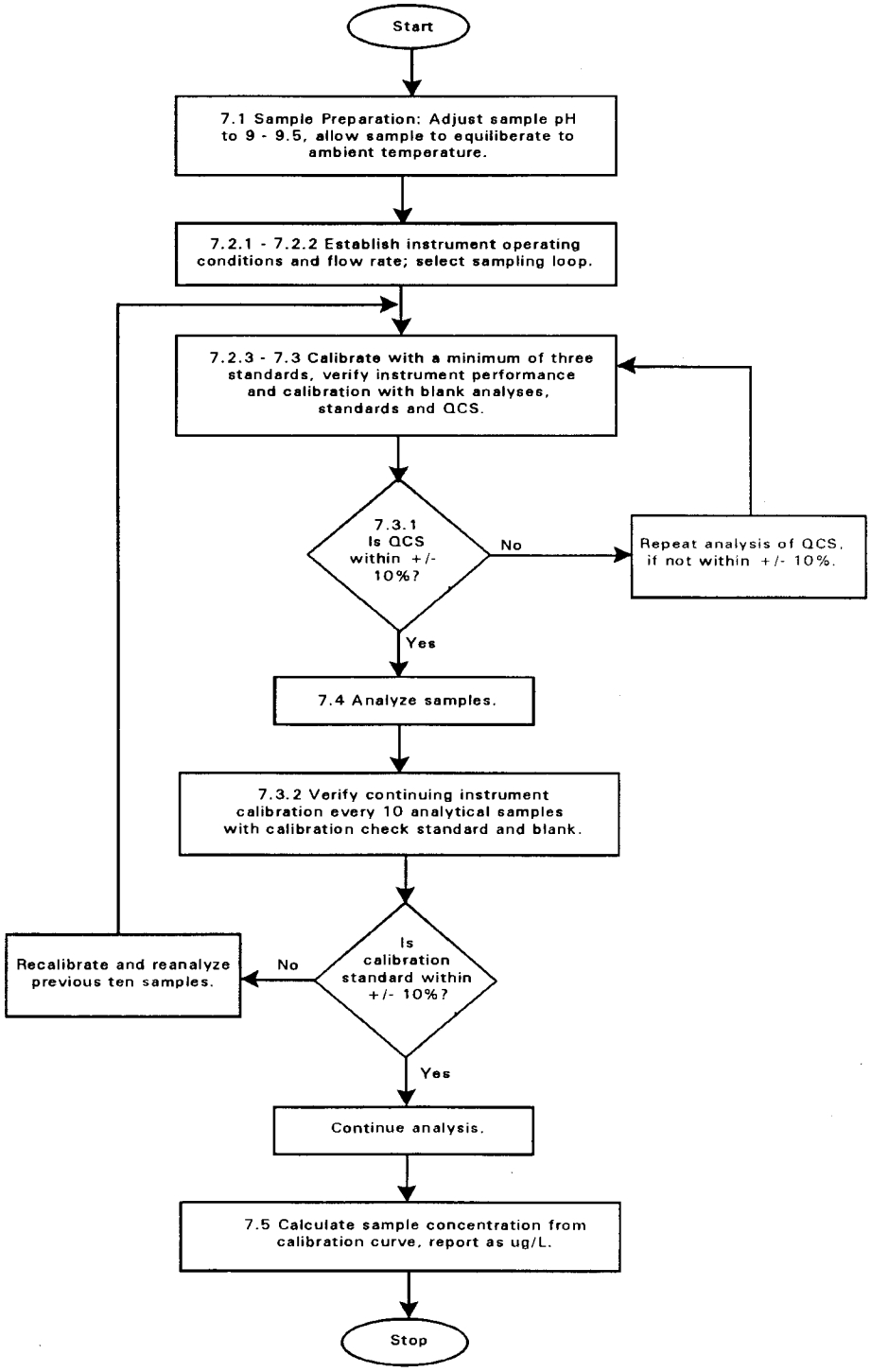


EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

MISCELLANEOUS ANALYTICAL METHODS

ANALYTICAL PROCEDURE FOR THE COLORIMETRIC DETERMINATION OF ETHYLENE GLYCOL AND FORMALDEHYDE

NYSDEC METHOD 89-9

1. Summary of Method

Ethylene glycol (1,2-Ethanediol) is converted to formaldehyde, which, in the presence of the reagents used, forms diacetyldihdrolutidine (DDL) and develops a yellow color to be read at 412 nm. Other glycols will also be detected by this procedure.

2. Apparatus and Materials

2.1 Balance - Analytical, capable of accurately weighing ±0.0001 g.

2.2 Vortex mixer.

2.3 Colorimeter - capable of utilizing a 5 cm sample cell and equipped to measure absorbances at 412 nm.

2.4 Water bath - capable of maintaining a temperature of 56° - 58°C.

2.5 Volumetric glassware.

2.6 Test tubes - 10 mL.

3. Reagents

3.1 Periodic acid, 0.02 M - dissolve 0.46 g H_5IO_6 in distilled, deionized water and dilute to 100 mL. Store in a dark bottle at 4°C. Discard after one month.

3.2 Iodide/thiosulfate solution - dissolve 2.59 g KI and 1.75 g $Na_2S_2O_3$ in distilled deionized water and dilute to 100 mL. Store at 4°C. Discard after two weeks.

3.3 Acetylacetone reagent - combine 15 g of ammonium acetate, 0.3 mL of glacial acetic acid, and 0.2 mL of 2,4-pentanedione and dilute to 100 mL with distilled deionized water.

3.4 Ethylene glycol stock solution (1% w/v)- dilute 0.9 mL of reagent grade ethylene glycol to 100 mL with distilled deionized water. 1 mL = 10,000 µg.

3.5 Formaldehyde stock solution - 37%, reagent grade. 1 mL = 370,000 µg.

4. Procedure

4.1 Prepare calibration standards from 0 to 10 ppm by serial dilutions of the stock solutions. One standard should be at or near the detection limit of the method.

4.2 Dispense 1.0 mL of each standard into separate test tubes as well as a blank of distilled deionized water. Dispense all samples, duplicates and spikes in duplicate. One sample in each analytical batch should be run in duplicate to assess precision and one sample in each batch should be spiked to assess recovery.

4.2 To each test tube containing 1.0 mL of standard, and one of the tubes for each sample or QC sample, add 0.5 mL of the periodic acid solution (Paragraph 3.1) to oxidize the glycol. Mix with the vortex mixer and let stand for 10 minutes. For the remaining test tube for each sample and QC sample, begin with Paragraph 4.4.

4.3 To each test tube add 0.5 mL of the iodide/thiosulfate solution (Paragraph 3.2) to neutralize any remaining periodic acid and vortex immediately.

4.4 To each tube add 2.0 mL of the acetylacetone reagent (Paragraph 3.3), vortex, and place in a 56°C - 58°C water bath for 10 minutes.

4.5 Remove tubes from water bath and allow to stabilize for 10 - 15 minutes. Read the absorbance at 412 nm. A detection limit of 100 ppb is achieveable using a 1 cm sample cell. By using a 5 cm sample cell a detection limit of 20 ppb is achieveable.

5. Calculations

5.1 Prepare a calibration curve from the standards that were analyzed. The curve should be linear from 0 - 10 ppm.

5.2 Calculate the concentration in all samples from the calibration curve.

5.3 For the analysis of glycols, the concentration of the unoxidized sample must be subtracted from the concentration of the oxidized sample to correct for any formaldehyde in the sample.

5.4 For the analysis of formaldehyde use the concentration of the unoxidized sample.

6. References

6.1 VanSlyke, D.D., Jour. Biol. Chem., 32, 455 (1917)

6.2 Somagyi, M., Jour. Biol. Chem., 160, 69 (1945)

6.3 Nash, T., Biochemical Journal, 55, 416 (1953)

ANALYTICAL METHOD FOR THE DETERMINATION OF PCB CONGENERS BY FUSED SILICA CAPILLARY COLUMN GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTOR (FSCC/GC/EC)

NYSDEC METHOD 91-11

SECTION I

INTRODUCTION

The analytical method that follows is designed to analyze aqueous samples for Polychlorinated Biphenyl Congeners.

The method is divided into the following sections: sample preparation, screening and analysis. Sample preparation covers sample extraction and cleanup techniques. As described in the screening section, a portion of the extracts may be screened on a gas chromatograph with appropriate detector to determine the concentration level of PCB congeners. The analysis section contains the fused silica capillary column gas chromatograph/electron capture detector (FSCC/GC/EC) method for PCB congeners.

1. Method for the Determination of PCB Congeners

1.1 Scope and Application

This method provides procedures for the determination of polychlorinated biphenyl congeners in aqueous samples. The method is applicable to samples containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. PCBs are identified and quantitated by congener. A concentration is determined for each PCB congener.

1.2 Summary of Method

The method involves solvent extraction of the matrix and analysis of the extract for PCB congeners on a fused silica capillary column gas chromatograph with electron capture detector (FSCC/GC/EC). If concentration permits, confirmation is to be done by GC/MS. Prior to sample analysis the method requires the laboratory to use individual congener standards to identify the retention time order of the resolvable congener peaks for each column that is used in the FSCC/GC/EC analysis. The Laboratory must also determine the method detection limit using FSCC/GC/EC for each of the resolvable PCB congener peaks. Table 1 is a list of all PCB congeners with their structure and associated Ballschmiter & Zell (BZ) numbers.

SECTION II

SAMPLE PREPARATION AND STORAGE

PART A - SAMPLE COLLECTION, PRESERVATION, STORAGE AND HOLDING TIMES

1. Sample Collection

1.1 Sample Containers

Samples must be collected in clean glass containers with Teflon®-lined caps. Do not rinse sample container with sample before filling.

1.2 Sample Preservation and Storage

The samples must be stored at 4°C (±2°C) from the time of receipt until extraction and analysis.

1.3 Holding Times.

Separatory funnel or continuous liquid-liquid extractions of water samples for PCB congener analyses, must be completed within SEVEN (7) days of sample collection. Analysis must be completed within FORTY (40) days of extraction.

1.4 Extract Storage

Sample extracts must be stored at 4°C, or less until analysis.

PART B - SAMPLE PREPARATION

1. Summary of Method

A measured volume of sample, approximately one-liter, is solvent extracted with hexane using a separatory funnel or a continuous liquid-liquid extractor. The hexane extract is concentrated in a Kuderna-Danish Evaporator, and adjusted to a final volume of 1 to 2 mL.

2. Interferences

2.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware that lead to false positive peaks and/or elevated baselines in gas chromatograms. All of the reagents and glassware used must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose a major problem in PCB congener analysis when using the electron capture detector. These compounds generally appear in the chromatogram as broadly eluting peaks. Common, flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of all plastics, except Teflon®, in the Laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination once it becomes a problem.

2.2 To minimize interferences, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Then wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry, dry in a 100°C oven or, if necessary, heat in a muffle furnace at 450°C for a few hours. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent. Volumetric glassware should not be heated in a muffle furnace.

2.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the site being sampled. The cleanup procedures in Part C, Extract-Cleanup Procedures, must be used to overcome such interferences to attempt to achieve the lowest detection limit possible. The sulfur cleanup procedures in Part C, Extract-Cleanup Procedures, may be used to remove sulfur interferences.

3. Safety

3.1 The toxicity or carcinogenicity of each chemical used in this method has not been precisely defined. Therefore, each should be treated as a potential health hazard and exposure should be reduced to the lowest feasible level. Each laboratory is responsilbe for safely disposing of materials and for maintaining awareness of OSHA regulations regarding safe handling of the chemicals used in this method. A reference file of material data handling sheets should be made available to all personnel involved in analyses. Additional information on laboratory safety is available (See Section VI).

4. Apparatus and Materials

4.1 Sampling Equipment

Sample Bottles - Meticulously cleaned (see Paragraph 2.2), 1 liter or larger amber glass fitted with Teflonâ-lined screw caps. (Bottles in which high purity solvents were received can be used as sample bottles without additional cleaning if they have been handled carefully to avoid contamination during and after use of original contents.)

4.2 Glassware (Brand names and catalog numbers included for illustration purposes only).

4.2.1 Graduated cylinder (1 L.)

4.2.2 Separatory funnel (2 L.)- with Teflon® stopcock.

4.2.3 Drying Column - glass column approximately 400 mm long x 19 mm ID, with coarse frit. (Substitution of a small pad of disposable, hexane washed Pyrex-glass wool for the frit will help prevent cross-contamination of sample extracts.)

4.2.4 Chromatographic column - glass column approximately 400 mm long x 19 mm ID, with coarse frit. (Substitution of a small pad of disposable, hexane washed Pyrex-glass wool for the frit will help prevent cross-contamination of sample extracts.)

4.2.5 Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

4.2.6 Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs or clips.

4.2.7 Snyder column - Kuderna-Danish, Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.8 Snyder column - Kuderna-Danish, Two-ball micro (Kontes K-569001-0219 or equivalent).

4.2.9 Continuous liquid-liquid extractors - Equipped with Teflon® or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor - Ace Glass Company, Vineland, NJ P/N 6841-10, or equivalent.)

4.2.10 Vials - Amber glass, 10 to 15 mL capacity, with Teflon®-lined screw caps.

4.2.11 Bottle or test tube - 50 mL with Teflon®-lined screw cap for sulfur removal.

4.2.12 Chromatographic column for Florisil - glass column approximately 400 mm long x 10 mm ID, with coarse frit. (Substitution of a small pad of disposable hexane washed, Pyrex-glass wool for the frit will help prevent cross-contamination of sample extracts.)

4.3 Pyrex-glass wool - to insure its cleanliness, pre-rinse glass wool with appropriate solvents.

4.4 Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with hexane.

4.5 Water or steam bath - Heated with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Balance - Analytical, capable of accurately weighing ±0.01 mg.

5. Reagents

5.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at greater than the MDL for each of the PCB congeners - distilled tap water is usually sufficiently pure.

5.2 Acetone, hexane - Pesticide quality or equivalent.

5.3 Sodium sulfate - (ACS) granular, anhydrous. Purify by Soxhlet extracting with hexane for 8 to 12 hours and drying in a vacuum oven or by heating in a muffle furnace at 450°C for 4 hours.

5.4 Florisil - Pesticide residue (PR) grade (60/100 mesh); purchase activated, or activate before use, at 1250°F (677°C) for 4 hours, stored in glass containers with ground-glass stoppers or foil-lined screw caps.

5.4.1 Deactivation of Florisil - Just before use. weigh out 1000 g of Florisil into a glass container and heat at 130°C for 16 hours. After heating, cool in a dessicator. Pour into a 4-L solvent bottle and dropwise add 40 mL of water while shaking to deactivate. Close with a Teflon®-lined cap and place on a tumbler or roller. Tumble for at least 4 hours. There should be no lumps present. Store in a tightly closed amber bottle. Let stand overnight before using.

5.4.2 Florisil Activity Check - Before each batch of Florisil is first used and once a week thereafter test the Florisil by adding 1 mL of GC/EC CAL STD-3 and following Part C, paragraph 1.2. All resolvable PCB congeners should be present in the extract after column elution.

5.5 Silicic acid (Mallinckrodt A.R. 100 mesh or equivalent). Before use, activate each batch at least 16 hours at 135°C in a shallow glass tray, loosely covered with aluminum foil.

5.6 Sodium hydroxide solution (10N). Dissolve 40 g NaOH (ACS reagent grade) in reagent water and dilute to 100 mL.

5.7 Tetrabutylammonium (TBA) - Sulfite reagent. Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL distilled water. To remove impurities, extract this solution three times with 20 mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon®-lined screw cap. This solution can be stored at room temperature for one month.

5.8 PCB surrogate standard spiking solution.

5.8.1 The surrogate standards are added to all samples, blanks, matrix spikes, and calibration standards before extraction. The surrogate compounds are tetrachloro-m-xylene and/or decachlorobiphenyl as specified in Table 2. Other surrogates may prove suitable, but it is the responsibility of the laboratory to demonstrate their acceptability.

5.8.2 Prepare the surrogate standard spiking solution at a concentration of 0.2 µg/1.00 mL of each of the two compounds in acetone. Store the spiking solutions at 4°C (±2°C) in Teflon®-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control

check samples indicates a problem. **CAUTION**: Analysts must allow all spiking solutions to equilibrate to room temperature before use.

5.9 Concentrated sulfuric acid-(ACS) (sp. gr. 1.84)

5.10 Sulfuric acid solution (1+1). Slowly add, with rapid stirring, 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

5.11 Potassium permanganate solution (5 percent w/v). Slowly add 100 mL of reagent water to 5 g of potassium permanganate in a Pyrex vessel.

5.12 Alkali solution - Prepare fresh daily as needed. Dissolve eight pellets of potassium hydroxide into 6 mL of ethanol in a glass stoppered test tube.

5.13 GPC calibration solution - prepare a solution in methylene chloride that contains the following analytes in concentrations listed below:

Analyte	mg/mL
corn oil	25
bis(2-ethylhexyl)phthalate	1.0
methoxychlor	0.2
perylene	0.02
sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

Store the calibration solution in an amber glass bottle with a Teflon®-lined screw-cap at 4°C, and protect from light. (Refrigeration may cause the corn oil to precipitate. Before use allow the calibration solution to stand at room temperature until the corn oil dissolves.) Replace the calibration standard solution every six months, or more frequently if necessary.

5.14 PCB Congener Matrix Standard Spiking Solution - Prepare a matrix spike standard solution that contains each of the congeners listed in Table 3 in acetone. Place each solution in a 10 - 15 mL clean glass vial with a Teflon®-lined screw-cap and store at 4°C (±2°C) and protect from the light. Stock solutions must be replaced after twelve months, or sooner if comparison with check standards indicates a problem. **CAUTION:** Each time a vial containing small volumes of solutions is warmed to room temperature and opened, a small volume of solvent in the vial headspace evaporates, significantly affecting

concentration. Solutions should be stored with the smallest possible headspace, and opening vials should be minimized.

Matrix spikes are also to serve as duplicates by spiking two 1-liter portions from the one sample chosen for spiking.

6. Sample Extraction - Separatory Funnel

6.1 Samples may be extracted using separatory funnel techniques. If emulsions prevent acceptable solvent recovery with separatory funnel extractions, continuous liquid-liquid extraction (Paragraph 7.) may be used. The separatory funnel extraction scheme described below assumes a sample volume of one liter.

6.2 Pour the entire sample into a 1-liter graduated cylinder to determine the sample volume then transfer to a 2-liter separatory funnel. (If a sample larger than 1 liter is extracted, the funnel size and solvent volume for samples and blanks must be adjusted also.) Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10N sodium hydroxide or 1:1 sulfuric acid solution. Pipet 1.0 mL of PCB surrogate standard spiking solution into the separatory funnel and mix well. Add 1.0 mL of PCB congener matrix spiking solution to each of two 1-liter portions from the sample selected for spiking.

6.3 Rinse the graduated cylinder with 60 mL of hexane and then transfer the solvent to the sample bottle and shake for two minutes, with periodic venting to release excess pressure. Transfer to the separatory funnel. Shake the separatory funnel for two minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means. Return the water layer to the sample bottle and collect the hexane layer in a 250 mL Erlenmeyer flask containing enough granular anhydrous sodium sulfate to allow for free flowing crystals. Swirl. When drying is complete, indicated by the clarity of the extract, decant the hexane phase into a 500 mL Kuderna-Danish evaporator with a 1 mL collection tube and three-ball Snyder column.

6.4 The aqueous layer is returned to the separatory funnel and the sample bottle and sample are extracted again as in Paragraph 6.3, the organic layer being collected in the Erlenmeyer flask, dried, and combined in the evaporator. Perform a third extraction in the same manner.

6.5 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL hexane to the top. Place the K-D apparatus on a hot water or steam bath so that the concentrator tube is partially immersed and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1.0 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE K-D TUBE TO GO DRY.

6.6 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. Reconnect the concentrator tube and concentrate the extract to a final volume of 1.0 mL.

6.7 Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the PCB congeners present in the calibration solutions. Nitrogen blow-down may be used with care, since its employment may result in intermittent loss of the more volatile PCB congeners.

6.8 Proceed to Part C, Extract-Cleanup Procedures.

7. Sample Extraction - Continuous Extractor

7.1 When experience with a sample from a given source indicates that a serious emulsion problem will result, or if an emulsion is encountered in Paragraph 6.3 using a separatory funnel, a continuous extractor may result in a successful extraction.

7.2 Pour the entire sample into a 1-liter graduated cylinder to determine the sample volume, then transfer to the continuous extractor. Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10N sodium hydroxide and/or 1:1 sulfuric acid solution. Rinse the graduated cylinder with 60 mL of hexane and then transfer the solvent to the sample bottle and shake for two minutes, with periodic venting to release excess pressure. Transfer to the continuous extractor. (If a sample larger than 1 liter is extracted, the size of the extractor and solvent volume for samples and blanks must be adjusted also.) Pipet 1.0 mL of PCB Surrogate Standard Spiking-Solution into the continuous extractor and mix well. Add 1.0 mL of PCB congener matrix spiking solution to each of two 1-liter portions from the sample selected for spiking.

7.3 Add 500 mL of hexane to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 hours. Allow to cool, then

detach the boiling flask and dry. Concentrate the extract as in Paragraphs 6.5 through 6.6.

7.4 Proceed to Part C, Extract-Cleanup Procedures.

PART C - EXTRACT-CLEAN-UP PROCEDURES

1. Florisil Cleanup

1.1 Add 10 g of Florisil to the Florisil chromatographic column. Tap the column to settle the Florisil. Add 2 g of granular anhydrous sodium sulfate.

1.2 Quantitatively transfer the 1-3 mL of hexane extract from Paragraph 7.3 to the top of the Florisil using a disposable Pasteur pipet.

1.3 Elute from the column with hexane and collect 50 mL of eluate in a 125 mL Erlenmeyer flask. Do not allow the column to go dry during the addition and elution of the sample. Transfer eluate from Erlenmeyer flask to K-D apparatus.

1.4 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL hexane to the top. Place the K-D apparatus on a hot water or steam bath so that the concentrator tube is partially immersed and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 10 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

1.5 Observe the appearance of the eluate.

1.5.1 If crystals of sulfur are evident or sulfur is expected to be present, proceed to Paragraph 2.

1.5.2 If additional cleanup is not indicated, proceed to Paragraph 7 - Final Extract Concentration.

2. Optional Sulfur Clean-up.

2.1 Transfer the 10. mL from paragraph 1.5 to a 50 mL clear glass bottle or vial with a Teflonâ-lined screw cap. Rinse the concentrator tube several times with 1.0 mL of hexane, adding the rinsings to the 50 mL bottle. If only a partial set of samples requires sulfur clean-up, set up a new reagent blank with 1.0 mL of hexane and take it through the sulfur clean-up. Include the surrogate standards.

2.2 Add 1 mL of TBA-sulfite reagent and 2 mL of 2-propanol, cap the bottle, and shake for at least 1 minute. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are

observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100 mg portions until a solid residue remains after repeated shaking.

2.3 Add 5 mL distilled water and shake for at least 1 minute. Allow the sample to stand for 5-10 minutes and remove the hexane layer (top) for analysis.

2.4 Alternatively, add 1 to 3 drops of mercury (10 - 30 µL) to the sample and seal. Agitate vial in a vortex mixer before quantitative transfer to the Florisil column. Activated copper powder may be substitued for mercury.

2.5 If further extract clean-up is not needed, proceed to Paragraph 7. - Final Extract Concentration. If further clean-up is needed proceed to Paragraph 3. - Optional Sulfuric Acid Clean-up.

3. Optional Sulfuric Acid Cleanup

3.1 Using a syringe or a volumetric pipette, transfer the hexane extract solution to a 10 mL vial and carefully add 5 mL of concentrated sulfuric acid. This procedure must always be done in a fume hood.

3.2 **CAUTION**: Make sure that there is neither an exothermic reaction nor evolution of gas prior to proceeding.

3.3 Cap the vial tightly and agitate using a vortex mixer for one minute. A vortex must be visible in the vial.

3.4 **CAUTION**: Stop agitating immediately if the vial leaks. **AVOID CONTACTING THE SOLUTION WITH BARE SKIN. SULFURIC ACID WILL BURN**.

3.5 Allow the phases to separate for at least one minute. Examine the top (hexane) layer. It should not be highly colored nor should it have a visible emulsion or cloudiness.

3.6 If a clean phase separation is achieved, proceed to Paragraph 3.10.

3.7 If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial via a glass pipette and dispose of it properly. Add another 5 mL of clean sulfuric acid.

3.8 **NOTE**: Do not remove any hexane at this stage of the procedure.

3.9 Agitate the sample using a vortex mixer and allow the phases to separate as described previously.

3.10 Transfer the hexane layer to a clean 10 mL vial.

3.11 Add an additional 1 mL of hexane to the sulfuric acid layer, cap the vial securely and shake. This second extraction is done to ensure quantitative transfer of all analytes.

3.12 Remove the second hexane layer and combine with the hexane from Paragraph 3.10.

4. Optional Permanganate Cleanup

4.1 Add 5 mL of the five percent aqueous potassium permanganate solution to the combined hexane fractions from Paragraph 3.12.

4.2 **CAUTION**: Make sure that there is neither an exothermic reaction nor evolution of gas prior to proceeding.

4.3 Cap the vial tightly and agitate using a vortex mixer for one minute. A vortex must be visible in the vial.

4.4 **CAUTION**: Stop agitating immediately if the vial leaks. **AVOID CONTACTING THE SOLUTION WITH BARE SKIN. POTASSIUM PERMANGANATE WILL BURN**.

4.5 Allow the phases to separate for at least one minute. Examine the top (hexane) layer. It should not be highly colored nor should it have a visible emulsion or cloudiness.

4.6 If a clean phase separation is achieved, proceed to Paragraph 4.10.

4.7 If the hexane layer is colored or the emulsion persists for several minutes, remove the permanganate solution from the vial via a glass pipette and dispose of it properly. Add another 5 mL of clean aqueous permanganate solution.

4.8 **NOTE**: Do not remove any hexane at this stage of the procedure.

4.9 Agitate the sample using a vortex mixer and allow the phases to separate as described previously.

4.10 Transfer the hexane layer to a clean 10 mL vial.

4.11 Add an additional 1 mL of hexane to the permanganate layer, cap the vial securely and shake. This second extraction is done to ensure quantitative transfer of all analytes.

4.12 Remove the second hexane layer and combine with the hexane from Paragraph 4.10.

5. Optional Silica Column Clean-up

5.1 If the clean-up of the extract will not be performed immediately, transfer the concentrate to a 10 mL Teflon®-lined screw-cap vial with a pasteur pipet (rinsing concentrator tube with several aliquots of hexane into the vial and store refrigerated.

5.2 Weigh 3.0 g portions of the dried silicic acid (Section ll, Part B, Paragraph 5.5) into vials and redry for 1 hour. When ready to prepare column, remove vial of silicic acid from oven and immediately seal with a Teflon®–lined cap. When the vial has cooled to room temperature, add 0.10 mL of water and then reseal. Mix contents thoroughly and let the adsorbent equilibrate for approximately one hour with occasional mixing.

Note: The silica column chromatography is included in the procedure to remove pesticides from the analysis. The optimum percent water on the silica used in the column chromatography must be determined by running standards. The percent water added to the activated silica should be adjusted to obtain optimum separation between PCBs and pesticides. For calibration purposes, a mixture of the PCB calibration standard with o,p'-DDT and p,p'-DDT may be used. The pesticides p,p'-DDE will not be separated from the PCB fraction. Under optimum conditions, not more than 20 - 60% of the o,p'-DDT will elute with the PCB fraction.

5.3 Empty the vial of equilibrated silicic acid into a chromatographic column and tap until the adsorbent is well settled. Top column with 1 - 2 cm prepared sodium sulfate.

5.4 Wash the column with 20 mL of methylene chloride, forcing solvent through the column at 2 - 3 mL per minute with approximately 6 psi nitrogen pressure. Stop the flow when the level of the solvent reaches the sodium sulfate layer. At this point, the silicic acid portion should have a uniform translucent appearance, without air pockets or channels.

5.5 Wash the methylene chloride from the column with 20 mL of hexane, again stopping the flow when the solvent level reaches the sodium sulfate layer. The column should have reverted back to its original opaque appearance.

5.6 Add the concentrated eluate from the Florisil column and rinse onto the column with heaxane.

5.7 Elute the column at 2 - 3 mL per minute with hexane, collecting the first 50 mL of eluate. Proceed to Paragraph 7. for final extract concentration.

6. Optional Gel Permeation Chromatography (GPC) Clean-up

6.1 GPC must be performed for water extracts that contain higher molecular weight contaminants that interfere with the analysis of the target analytes. Gel permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules. The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated. A cross-linked divinyl benzenestyrene copolymer (SX-3 Bio Beads or equivalent) is specified for this method.

GPC is recommended for the elimination from the sample of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds. GPC is appropriate for both polar and non-polar analytes, therefore, it can be used effectively to clean up extracts containing a broad range of analytes.

Normally, this method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph (GC) or in the front of the GC column. This residue ultimately will reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. Pentachlorophenol especially is susceptible to this problem. GPC system performance must be validated at least once every seven calendar days by demonstrating 80-110 percent recovery of the pesticide matrix spike mixture and examining the pattern of peaks from an Aroclor 1016/1260 mixture.

6.2 GPC columns may be purchased prepared of the following preparation procedure must be used.

6.2.1 Weigh out 70 gm of Bio Beads (SX-3). Transfer them to a 1 liter bottle with a Teflon®-lined cap or a 500 mL separatory funnel with a large bore stopcock, and add approximately 300 mL of methylene chloride.

Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 2 hours. Maintain enough solvent to cover the beads sufficiently at all times. If a guard column is to be used, repeat the above with 5 gm of Bio Beads in a 125 mL bottle or a beaker, using 25 mL of methylene chloride.

6.2.2 Turn the column upside down from its normal position, and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near

the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

6.2.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

6.2.4 Swirl the bead/solvent slurry to get a homogeneous mixture and, if the wetting was done in a quart bottle, quickly transfer it to a 500 mL separatory funnel with a large bore stopcock. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached), and allow the excess solvent to drain. Raise the tube to stop the flow, and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

6.2.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

6.2.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat the step in Paragraph 6.2.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is inserted successfully.

6.2.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

6.2.8 Pack the optional 5 cm column with approximately 5 gm of preswelled beads (different guard columns may require different amounts). Connect the guard column to the inlet of the analytical column.

6.2.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube will force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel tubing of 1/16" OD x 10/1000" ID x 2". Pump methylene chloride through the column at a rate of 5 mL/min for one hour.

6.2.10 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as the one in Paragraph 6.2.9) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

6.2.11 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify retention volumes have not changed.

NOTE: The description of solvent flow rate and column pressure applies only to the ABC GPC apparatus. Laboratories using equivalent equipment must develop the parameters for their apparatus which give acceptable performance as described in Paragraph 6.4.

6.2.12 The GPC calibration procedure is based on monitoring the elution of standards with a UV detector connected to the GPC column.

Care must be taken to account for any difference in volume (elution time) between the GC column and the detector and between the GPC column and the collection vial.

NOTE: The UV detector calibration procedure described in Paragraph 6.3 is to be used for the analyses of organochlorine pesticides and Aroclors listed in Exhibit C. IT MUST NOT BE USED FOR THE ANALYSIS OF GC/MS EXTRACTABLES OR OTHER ANALYTES WITHOUT A RECOVERY STUDY.

6.3 Calibration of the GPC Column

6.3.1 Using a 10 mL syringe, load sample loop #1 with calibration solution (Paragraph 5.13). With the ABC automated system, the 5 mL sample loop requires a minimum of 8 mL of the calibration solution. Use a firm, continuous pressure to push the sample onto the loop. Switch the valve so that GPC flow is through the UV flow-through cell.

6.3.2 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace that meets the following requirements. Differences between manufacturer's cell volumes and detector sensitivities may require a dilution of the calibration solution to achieve similar results. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell and, therefore, the analytical cell is not acceptable for use.

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

6.3.3 Determine the elution times for the phthalate, methoxychlor, and perylene. Phthalate will elute first, perylene, last.

6.3.4 Choose a "DUMP" time which removes >85 percent of the phthalate. Choose a "COLLECT" time so that >95 percent of the methoxychlor is collected, and continue to collect until just prior to the elution time of sulfur. Use a "WASH" time of 10 minutes.

6.3.5 **NOTE:** The DUMP and COLLECT times must be adjusted to compensate for the difference in volume of the lines between the detector and the collection flask.

6.3.6 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45 - 55 mL (4.5 - 5.5 mL/min). If the flow rate is outside of this range, corrective action must be taken to achieve this flow rate. Once the flow rate is within the range of 4.5 - 5.5 mL/min, record the column pressure (should

be 6 - 10 psi) and room temperature. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared. A UV trace that does not meet the criteria in Paragraph 6.3.2 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

6.3.7 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

6.3.7.1 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

6.3.7.2 The retention times for bis(2-ethylhexyl)phthalate and perylene must not vary more than ±5% between calibrations. If the retention time shift is >5%, take corrective action. Excessive retention time shifts are caused by the following:

- Poor laboratory temperature control or system leaks.
- An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.
- Excessive laboratory temperatures causing outgassing of the methylene chloride.

6.3.8 Analyze a GPC blank by loading 5 mL of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using a Kuderna-Danish (K-D) evaporator.

Exchange the solvent to hexane and analyze the concentrate by GC/EC. If the blank exceeds one half the CRQL of any analyte, assuming that the blank represents the extract from a one liter water sample, pump additional methylene chloride through the system for 1 - 2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

6.4 GPC Calibration Check

No Florisil cleanup is used in the GPC calibration check.

6.4.1 At least once every 7 days, the calibration of the GPC must be verified with two check mixtures. The first mixture is prepared by concentrating 2.0 mL of the matrix spiking solution (Paragraph 5.14) to less than 1 mL, and adjusting the final volume to 10.0 mL with methylene chloride. The second mixture is prepared with 2 µg of Aroclor 1016 and 2 µg of Aroclor 1260 in a final volume of 10.0 mL methylene chloride.

6.4.2 Load the first 5.0 mL sample loop by using a 10 mL syringe containing 8 mL of the diluted pesticide matrix spike solution (Paragraph 6.4.1). The Aroclor mixture is loaded into Loop 2 in the same manner. Fractions are collected in an auto sequence by using the GPC program established by the UV detector calibration procedure (Paragraph 6.3).

6.4.3 The collected GPC calibration fraction is transferred to a K-D apparatus, and the collection vessel is rinsed with two additional 10-mL portions of methylene chloride to complete the transfer. The volume of methylene chloride is reduced (described in Paragraph 7.). After cooling, the solvent is exchanged to hexane according to the instruction in Paragraph 6.2. The final volume is adjusted to 10.0 mL, and the sample is analyzed by GC according to the procedures in Section lll. The analysis must be performed on at least one of the GC columns used for samples analysis.

6.4.4 The pattern of the Aroclor quantitation peaks and the recovery of each single component analyte must be determined for evaluation and reporting purposes. If the recovery of each of the single component analytes is 80 to 110 percent and if the Aroclor pattern is the same as with previously run standards, then the analyst may continue to use the column. If recoveries are out of the acceptance window or if changes in the relative peak heights of the patterns of the Aroclor are observed, the column must be replaced and recalibrated according to the instructions in Paragraph 6.3.

6.4.5 Some samples may contaminate the SX-3 Bio Beads and change the retention volume of the GPC column. Therefore system calibration and analyte recovery must be checked whenever a sample causes significant discoloration of the GPC column. Even if no darkening is visible, GPC calibration must be checked not less than once every seven days. In many cases, the SX-3 Bio Beads may be used for several months as long as the column calibration and flow rate remain constant.

6.5 Daily UV calibration check (optional).

The calibration of the GPC may be monitored daily by use of the UV-GPC calibration solution (Paragraph 4.9.3) and the UV Detector Calibration Procedure (Paragraph 6.3). The UV detector should be used to monitor the elution times

for the phthalate, methoxychlor, and perylene, in that order. The precalibrated GPC program should "DUMP" >85 percent of the phthalate and should "COLLECT" >95 percent of the methoxychlor and perylene. Significant changes in elution times of the analytes (e.g., >0.5 minutes) indicate that the column is out of calibration and must be recalibrated or replaced.

6.6 Sample Extract Cleanup

It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined by the calibration standard no longer will be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22°C.

6.6.1 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution must be diluted and loaded into several loops. Similarly, extracts containing more than 500 mg of nonvolatile residue per 5 mL of extract must be diluted and loaded into several loops. The nonvolatile residue may be determined by evaporating a 100 µL aliquot of the extract to dryness in a tared aluminum weighing pan, or other suitable container.

6.6.2 Particles greater than 5 micron may scratch the valve, which may result in a system leak and cross contamination of sample extracts in the sample loops. To avoid such problems, filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container, e.g., a 15 mL culture tube with a Teflon®-lined screw cap. Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. Draw a minimum of 8 mL of extract into a 10 mL syringe. INTRODUCTION OF PARTICULATES OR GLASS WOOL INTO THE GPC SWITCHING VALVES MAY REQUIRE FACTORY REPAIR OF THE APPARATUS.

6.6.3 Prior to loading samples, put the GPC into the "LOAD" mode, set the instrument terminal for the number of loops to be loaded, and set the "DUMP", "COLLECT", and "WASH" times for the values determined by the calibration procedure described in Paragraph 6.3.

6.6.4 Attach the syringe to the turn lock on the injection port. Use firm, continuous pressure to push the sample onto the 5-mL sample loop. If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action. If the back pressure is normal (6 - 10

psi) the blockage is probably in the valve. Blockage may be flushed out of the valve by reversing the inlet and outlet tubes and pumping solvent through the tubes (this should be done before sample loading).

NOTE: Approximately 2 mL of the extract remains in the lines between the injection port and the sample loop; excess sample also passes through the sample loop to waste.

6.6.5 After loading a loop, and before removing the syringe from the injection port, index the GPC to the next loop. This will prevent loss of sample caused by unequal pressure in the loops.

6.6.6 After loading each sample loop, wash the loading port with methylene chloride in a PTFE wash bottle to minimize cross contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

6.6.7 After loading all the sample loops, index the GPC to the OO position, switch to the "RUN" mode (or follow the manufacturer's directions) and start the automated sequence. Process each sample using the collect and dump cycle times established in Paragraph 6.3.

6.6.8 Collect each sample in a 250-mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a Kuderna-Danish evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

- Change in solvent flow rate, caused by channeling in the column or changes in column pressure.

- Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.

- Leaks in the system or significant variances in room temperature.

6.6.9 After the appropriate GPC fraction has been collected for each sample, the solvent must be exchanged to hexane as described in Paragraph 6.2.

6.6.10 Any samples that were loaded into two or more loops must be recombined before proceeding to Paragraph 6.7.

6.7 Solvent exchange into hexane

This procedure applies to both extracts of water samples and extracts of soil samples.

6.7.1 With the extract in a K-D apparatus, remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as described previously. When the apparent volume of liquid reaches 3 to 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. DO NOT ALLOW THE EVAPORATOR TO GO DRY.

6.7.2 Remove the Snyder column; using 1 to 2 mL of hexane, rinse the flask and its lower joint into the concentrator tube. Complete quantitative transfer of the extract to a 10 mL vial by using hexane.

6.7.3 For samples which have not been subjected to GPC cleanup, adjust the volume of the hexane extract to 10.0 mL. For samples which have been subjected to GPC cleanup, concentrate the hexane extract to 5.0 mL using the procedure described in Paragraph 7. Proceed to Paragraph 1. for Florisil cartridge cleanup.

7. Final Extract Concentration

7.1 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL hexane to the top. Place the K-D apparatus on a hot water or steam bath so that the concentrator tube is partially immersed and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.2 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. Reconnect the concentrator tube and concentrate the extract to a final volume of 1.0 mL. Transfer the 1.0 mL to a GC vial and label as PCB fraction. The extract is ready for GC/EC analysis. Proceed to Section III - FSCC/GC/EC Analysis of PCBs. Store the extracts at 4°C (±2°C) in the dark until analyses are performed.

7.3 Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all the PCB congeners present in Calibration Standard #3. Air or nitrogen blow-down is not recommended since its employment results in intermittent loss of the more volatile PCB congeners.

SECTION III

FSCC/GC/EC ANALYSIS OF PCB CONGENERS

1. Summary

1.1 The hexane extracts of water are analyzed on a fused silica capillary column gas chromatograph equipped with an electron capture detector (FSCC/GC/EC). If PCB congeners are tentatively identified, a second GC/EC analysis is recommended using an alternate column.

2. Interferences

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

3. Apparatus and Materials

3.1 Gas chromatograph - An analytical system complete with gas chromatograph and all required accessories including syringes, analytical columns, gases, electron capture detector, and strip-chart recorder with recording integrator.

3.1.1 Quantitation and/or confirmation columns.

3.1.1.1 Capillary Column 1 - 40 m x 0.18 mm ID, 0.4 micron film thickness, fused silica capillary column (J&W Scientific DB-5 or equivalent).

3.1.1.2 Capillary Column 2 - 60 m x 0.25 mm ID, 0.25 micron film thickness, fused silica SP-2100, splitless mode

3.1.2 A data system capable of handling information on the congener peaks is required for measuring peak areas or peak heights, recording retention times, and calculating data.

3.2 Balance-analytical capable of accurately weighing ±0.01 mg.

4. Reagents

4.1 Hexane, acetone and toluene - Pesticide quality or equivalent.

4.2 Stock standard solution - prepared from the individual congener standards that are commercially available.

Prepare a stock standard solution of each of the PCB congeners listed in Table 4 and any additional individual PCB congeners that the laboratory has identified to be resolvable and commercially available. These should be at a concentration 10,000 times more concentrated than Calibration Standard #1 (Paragraph 4.4.1). (The 10,000 times statement is based on the criteria that a reliable weighting of a neat congener on an analytical balance be at least 1 milligram which is then diluted to 10 mL. The 6 - 7 aliquots can be ampouled as stock solutions to assure backup standards are readily available. On the other hand, commercially available standards of solutions of congeners should be acceptable as stock standards if a reliable supplier can be identified.) Place the solution in a clean glass vial with a Teflon®-lined screw cap and store at 4°C (±2°C) and protect from the light. The stock solution must be replaced after twelve months, or sooner if comparison with check standards indicates a problem.

4.3 Primary Dilution Standard Solution - Accurately measure 100 µL aliquots of the PCB congener stock solution (Paragraph 4.2) and dilute to 10 mL in a volumetric flask with hexane.

4.4 Calibration Standard Solutions - Prepare calibration standards, diluted from the Primary Dilution Standard Solution (Paragraph 4.3) with hexane, at a minimum of 5 concentrations levels, such that Calibration Standard #1 contains each of the appropriate PCB congeners at a concentration 3 - 5 times the MDL for that congener. Include the tetrachloro-m-xylene and/or decachlorobiphenyl surrogates in each standard. Table 4 is a suggested list of PCB congeners to be used that are currently available. Additional congeners may be added to the mixture as they become available. Place each solution in a clean glass vial with a Teflon®-lined screw cap and store at 4°C (±2°C) and protect from the light.

4.4.1 Calibration Standard #1 (CAL STD-1) - dilute 100 µL of the Primary Dilution Standard Solution to 10 mL using hexane.

4.4.2 Calibration Standard #2 (CAL STD-2) - dilute 200 µL of the Primary Dilution Standard Solution to 10 mL using hexane.

4.4.3 Calibration Standard #3 (CAL STD-3) - dilute 400 µL of the Primary Dilution Standard Solution to 10 mL using hexane.

4.4.4 Calibration Standard #4 (CAL STD-4) - dilute 600 µL of the Primary Dilution Standard Solution to 10 mL using hexane.

4.4.5 Calibration Standard #5 (CAL STD-5) - dilute 800 µL of the Primary Dilution Standard Solution to 10 mL using hexane.

4.5 MDL Standard Solutions - Prepare 5 to 10 standards of all of the PCB congeners in the calibration standards, such that each contains a maximum

of 20 fully resolvable (chromatogram must return to baseline between each peak) of the appropriate PCB congeners at a concentraction 30 - 50 times the estimated MDL for that congener. Table 4 is a suggested list of PCB congeners to be used that are currently available. Additional congeners may be added to the mixtures as they become available. Place each solution in a clean glass vial with a Teflon®-lined screw cap and store at 4°C (±2°C) and protect from the light.

5. Initial Calibration

5.1 The gas chromatographic system must initially be calibrated using the external standard technique for all columns used for quantitation. Table 5 provides operating conditions for the gas chromatograph.

Tables 6 and 7 list the identification and the typical relative retention times for the resolvable peaks using these columns. These are provided for information only. The Laboratory must determine the relative retention times for these peaks for the specific analytical system used.

5.2 External standard calibration procedure:

5.2.1 Prepare calibration standards as described in Paragraph 4.4 above.

5.2.2 Inject 1 to 2 µL of the standard extract using the solvent-flush technique or auto samplers. Smaller volumes can be injected only if automatic devices are employed. Record the volume injected to the nearest 0.05 µL and the total extract volume.

5.2.3 Inject each of the five Calibration Standards and a hexane blank. To establish the RT window for the PCB congener peaks, use the mean of the absolute RT from the above chromatograms as the mid-point, and ±3 times the standard deviation as calculated below for each congener. CAL STD-3 is analyzed intermittently throughout the analysis. Any PCB congener outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all affected samples. Tabulate peak height or area responses against the mass injected for each Calibration Standard. The results can be used to prepare a calibration curve for each PCB congener peak. A first or second order regression equation may be used to fit to the data. No higher order of regression is allowed. The correlation coefficient must be >0.990. A plot of the calibration curve and standards must be supplied with the sample results.

SD = Standard Deviation of the retention time for each congener

Where:

$$SD = \sqrt{\frac{\sum_{i=1}^{N}\left(x_i - \overline{x_i}\right)^2}{N - 1}}$$

x_i = mean retention time for congener(i)

NOTE: Use of a computerized statistical data package is highly recommended, with the data being electronically transmitted to the computer from the GC.

5.2.4 This should be done on each quantitation column and each instrument before any samples are analyzed by this procedure, each time a new column is installed, or whenever quality control samples indicate a calibration problem.

5.2.5 This full range calibration must be done whenever significant adjustments to the GC system are made (e.g., column changes, cleaning or changing the detector).

6. Method Detection Limit (MDL) Determination

6.1 Prepare seven low level PCB congener MDL standards by spiking a seven liter volume of reagent water with 700 µL of the PCB congener matrix spiking solution (see Paragraph 4.5 of this Section).

6.2 Extract these low level PCB MDL standards following the procedures in Section II, Part B.

6.3 Analyse the low level PCB MDL standards as described in Paragraph 7 of this Section.

6.4 Calculate the standard deviation of the results for each congener for the seven analyses as follows:

SD = Standard Deviation of the retention time for each congener

Where:

$$SD = \sqrt{\frac{\sum_{i=1}^{N}\left(x_i - \overline{x_i}\right)^2}{N - 1}}$$

x_i = mean retention time for congener(i)

N = 7

6.5 Calculate the MDL for each congener as follows:

MDL = 3.14 x SD

7. FSCC/GC/ECD Primary Analysis

(Quantitation may be performed on primary or confirmation analyses).

7.1 Sample analysis of extracts from Section II, Sample Preparation, can begin when linearity QA/QC requirements specified in Section IV, Paragraph 5.3.2.3 have been met.

Analyze samples in groups of no more than 5 samples. After the analysis of each group of up to 5 samples, analyze CAL STD-3. The PCB analytical sequence must end with CAL STD-3 regardless of the number of samples analyzed (see Paragraph 7.1.4).

If the samples are split between 2 or more instruments, the complete set of standards must be analyzed on each instrument with the same calibration requirement. All standards must be analyzed prior to the samples to avoid the effects of poor chromatography caused by the unsuspected injection of a highly concentrated sample.

7.1.1 Paragraph 7.1.1.1 contains GC performance criteria. If it is determined during the course of the analytical sequence that one or more of the criteria have been violated, stop the run and take corrective action. After corrective action has been taken, the analytical sequence may be restarted as follows. If a standard violated the criterion, restart the sequence with the previous standard, determine that the criteria have been met and continue with sample analyses, according to Paragraph 7.1.4. If a sample violated the criterion, restart the sequence with the standard that preceeded that group of samples (thereby preserving the sequence of standards in Paragraph 7.1.4), determine that the criteria have been met and continue with sample analysis, according to Paragraph 7.1.4.

If it is determined after completion of a analytical run that one or more criteria have been violated, proceed as follows. If a standard violated the

criterion, all samples analyzed after the previous good standard must be re-analyzed as part of a new analytical sequence. If a subsequent standard in the original sequence met all the criteria, then only those samples analyzed between the standard previous to the standard that did not meet the criterion and the standard that did meet the criterion must be re-analyzed as part of a new analytical sequence. If only samples violated the criteria, then those samples must be re-analyzed as part of a new analytical sequence.

7.1.1.1 Differences in the Calibration Factors for each CAL STD-3 must not exceed 15.0% during the Primary Analysis. Calculate % difference using the initial CAL STD-3 versus all subsequent CAL STD-3 analyzed during the analytical sequence. **NOTE**: To determine that no PCB congeners are present at or above the practical quantitation limit is a form of quantitation.

The retention time shift of the tetrachloro-m-xylene and decachlorobiphenyl surrogates in any standard or sample must be less than 0.3% difference.

7.1.2 Inject 1 to 2 µL of the sample or standard extract using the solvent-flush technique or auto samplers. Smaller volumes can be injected only if automatic devices are employed. Record the volume injected to the nearest 0.05 µL and the total extract volume.

7.1.3 The analytical sequence must be asdescribed in Table 8.

7.1.4 Inject the method blank (extracted with each set of samples) on every GC and GC column on which samples are analyzed.

7.2 Evaluation of Chromatograms

7.2.1 Consider the sample negative when all PCB congener peaks, depending on the congener's response factor, results in concentration less than the method detection limit. The sample is complete at this point. Confirmation is not required.

7.2.2 Tentative identification is when the unknown's retention time matches the retention time of a corresponding standard congener peak from the previous CAL STD-3.

7.2.3 Determine if any PCB congeners are present.

7.2.3.1 If the response for any of these compounds is less than or equal to the response of CAL STD-5, the extract is ready for confirmation and quantitation.

7.2.3.2 If the response for any compound is greater than the response for CAL STD-5, dilute the extract so that the peak will be approximately midway in the calibration range and reanalyze. Use this dilution also for confirmation and quantitation.

7.2.4 Quantitation may be performed on the primary analysis. See Section IV for special QC requirements for quantitation.

7.2.5 If identification of compounds of interest are prevented by the presence of interferences, further clean-up is required.

7.2.6 When selecting a GC column for confirmation and/or quantitation, be sure as few as possible of the PCB congeners to be confirmed/quantitated overlap. When samples are very complex, it may be necessary to use more than two columns to achieve adequate separation (>25% resolution) for as many as possible of the PCB congeners being quantitated. Two recommended capillary columns are listed in Table 4. The analyst should be aware that coeluting PCB congeners on one column may coelute with different PCB congeners on a different column.

8. GC/EC Confirmation Analysis

8.1 Confirmation Analysis is performed to confirm the identification and quantification of all PCB congeners tentatively identified in the Primary Analysis.

8.2 Table 4 provides examples of operating conditions for the gas chromatograph. All QC specified in Section IV must be adhered to, i.e., the specified criteria for degradation, linearity, calibration factor for standards, and retention time shift for tetrachloro-m-xylene and/or decachlorobiphenyl. Apply instructions from Paragraph 6.1.3 to the confirmation analysis.

8.3 Inject 1-2 µL of the sample or reagent blank extract and standards using the solvent-flush technique or auto samplers. A volume of 1 µL can be injected only if automatic devices are employed. Record the volume injected to the nearest 0.05 µL and the total extract volume. The detector attenuation must provide peak response equivalent to the Primary Analysis response for each compound to be confirmed.

8.3.1 Begin the Confirmation Analysis GC sequence with the five concentration levels of the CAL STDs.

8.3.2 After injection of the calibration standards, begin injection of samples. Analyze groups of 5 samples. Analyze CAL STD-3 after the first group of 5 samples followed by the analysis of another CAL STD-3. Continue analyzing groups of 5 samples, alternately analyzing a CAL STD-3 between groups of 5 samples. The alternating CAL STD-3 calibration

factors must be within 15.0% of each other if quantitation is performed. Deviations larger than 15.0% require the laboratory to repeat the analyses of samples which were analyzed after the standard that exceeded the criterion. The 15.0% criterion only pertains to compounds being quantitated.

If the samples are split between 2 or more instruments, all required calibration standards and the method blanks pertaining to those samples must be analyzed on each instrument.

8.3.3 Inject the method blank (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

8.4 Evaluation of Chromatograms

8.4.1 A compound tentatively identified in the primary analysis is confirmed if the retention time from the confirmation analysis falls within the retention time window of a corresponding standard that was chromatographed on the same instrument within an analytical sequence.

8.4.2 Quantitation must be performed and reported on all columns used for PCB congener identification. **NOTE**: To determine that no PCB congeners are present at or above the method detection limit is a form of quantitation.

8.4.3 If identification of compounds of interest are prevented by the presence of interferences, further cleanup is required. If sulfur is evident go to Sulfur Cleanup (Section II, Part C, Paragraph 2).

If unknown interferences or poor chromatography are noted only in the sample chromatogram, extract cleanup procedures (Section II, Part C) should be applied.

8.4.4 Calculate surrogate standard recovery on all samples, blanks, and spikes unless the surrogate was diluted out. See formula for calculation in Paragraph 9.3.

8.4.5 If PCB congeners were identified in the unspiked sample from which the matrix spike and matrix spike duplicate were prepared, confirmation analysis is required for the matrix spike and matrix spike duplicate. If PCB congeners were not identified in the unspiked sample, confirmation of the matrix spike and matrix spike duplicate is not required. Calculate matrix spike duplicate recoveries.

9. Calculations

9.1 Calculate the concentration in the sample using the following equation for external standards. Response can be measured by the manual peak height technique or by automated peak height or peak area measurements from an integrator.

$$\text{Concentration of each congener } C_x\ (\mu g/L) = \frac{(A_x)(I_s)(V_t)}{(A_s)(V_i)(V_s)}$$

Where:

A_x = Response for the parameter to be measured.

A_s = Response for the external standard.

V_t = Volume of total extract (µL) (take into account any dilutions).

I_s = Amount of standard injected in nanograms (µg).

V_i = Volume of extract injected (µL).

V_s = Volume of water extracted (L).

9.2 Match retention times of peaks in the standards with peaks in the sample. Calculate the concentration of every identifiable congener peak unless interference with individual peaks persist after cleanup.

9.3 Calculation for surrogate and matrix spikes recovery.

$$\text{Percent Recovery} = \frac{Q_d \times 100\%}{Q_a}$$

Where:

Q_d = quantity determined by analysis

Q_a = quantity added to sample.

Be sure all dilutions are taken into account.

9.4 Report results in micrograms per liter without correction for recovery data. If the concentration for any resolvable PCB congener peak, as calculated using the secondary column analysis, differs by greater than ±25% from the value calculated using the primary column, report the lower concentration result, qualified with a "P" flag.

SECTION IV

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

1. Introduction

This section outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with the determination of PCB congeners in aqueous samples. These QC operations are as follows:

- Method Blank Analysis
- Surrogate Spike Response Monitoring
- Matrix Spike and Matrix Spike Duplicate Analysis
- Specific QA/QC for PCB Calibration, Quantitation, and Confirmation

2. Method Blank Analysis

A method blank is a volume of deionized, distilled laboratory water , carried through the entire analytical scheme (extraction, concentration, and analysis). The method blank volume must be approximately equal to the sample volumes being processed.

2.1 Method blank analysis must be performed at the following frequency:

- each 20 samples in a Sample Delivery Group that are of similar matrix, OR

- whenever 20 or fewer samples from the same Sample Delivery Group are extracted by the same procedure (separatory funnel or continuous extraction),

whichever is more frequent, on each GC system used to analyze samples.

2.2 It is the Laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

2.2.1 For the purposes of this Protocol, an acceptable laboratory method blank must contain no PCB congener at or above the MDL determined by the laboratory

2.2.2 If a laboratory method blank exceeds these criteria, the Laboratory must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) MUST be reextracted and reanalyzed.

The reextraction should be performed within the 7 days of sample collection, whenever possible. The Laboratory Manager, or his designee, must address problems and solutions in a Case Narrative.

2.3 Documentation

The Laboratory must report results of method blank analysis.

2.3.1 The Laboratory must report ALL sample concentration data as UNCORRECTED for blanks.

3. Surrogate Spike (SS) Analysis

Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before purging or extraction in order to monitor preparation and analysis of samples.

3.1 Each sample, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown in Table 2 are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocols will not be permitted.

3.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the advisory recovery limits of 60 to 150 percent for both suggested surrogate compounds. If the laboratory uses different surrogate compounds, recovery should be evaluated against statistical limits developed from the laboratory's historical data. The Laboratory should also keep a historical record of the area counts for the surrogate compounds, and evaluate the system performance based on a statistical evaluation of the historical data.

3.3 Documentation

The Laboratory shall report surrogate recovery data for the following:

- Method Blank Analysis
- Sample Analysis
- Matrix Spike/Matrix Spike Duplicate Analyses

4. Matrix Spike/Matrix Spike Duplicate Analysis (MS/MSD)

In order to evaluate the matrix effect of the sample upon the analytical methodology, the PCB congener matrix spiking solution described in Section II, Part B, Paragraph 5.12 is to be used for matrix spike and matrix spike duplicate analyses. These compounds are subject to change depending upon availability and suitability for use as matrix spikes.

4.1 MS/MSD Frequency of Analysis

A matrix spike and matrix spike duplicate must be performed on a sample once:

- each 20 samples in a Sample Delivery Group of a similar matrix, OR
- each 7 calendar day period during which samples in a Sample Delivery Group were received (said period beginning with the receipt of the first sample in that Sample Delivery Group),

whichever is most frequent.

4.2 The analytical protocols in Section II stipulate the amount of matrix spiking solution to be added to the sample aliquots prior to extraction. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples.

4.2.1 Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

4.3 Individual component recoveries of the matrix spike are calculated using the following equation:

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Spike Sample Results

SR = Sample Result

SA = Spiked Added from spiking mix

4.4 Relative Percent Difference (RPD)

The Laboratory is required to calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using the following equation.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = Relative Percent Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

4.5 Documentation

The matrix spike (MS) results (concentrations) for nonspiked PCB congeners shall be reported along with the matrix spike percent recoveries. This will assist data users in assessing analytical precision of non-spiked congeners.

5. PCB Calibration, Quantitation, and Confirmation QA/QC Requirements

Paragraph 5 summarizes ongoing QC activities involved with PCB congener analysis that were detailed in Paragraphs 1, 2, 3, and 4 of this Section, and describes the additional QA/QC procedures required during the analysis of PCB congeners that are not covered in Paragraphs 1,2, 3, and 4.

5.1 The Laboratory must perform the following:

5.1.1 Method Blank analysis as per Paragraph 1 of this Section.

5.1.2 Spike all standards, samples, blanks, matrix spike and matrix spike duplicate samples with the surrogate spike compounds (tetrachloro-m-xylene and/or decachlorobiphenyl) as per Paragraph 2 of this Section.

5.1.3 Matrix Spike/Matrix Spike duplicate analysis as per Paragraph 3 of this section.

5.2 The external standard quantitation method must be used to quantitate all parameters. Before performing any sample analysis, the laboratory is required to determine the retention time window for each PCB congener to be determined and the surrogate spike compounds. These retention time windows are used to make tentative identification of the PCBs during sample analysis.

5.2.1 Establish retention time windows as follows:

CAL STD-3 is analyzed intermittently throughout the analysis. Any PCB congener outside of its established retention time window requires immediate investigation and correctionbefore continuing the analysis. The laboratory must reanalyze all affected samples. Tabulate peak height or area responses against the mass injected for each Calibration Standard. The results can be used to prepare a calibration curve for each PCB congener peak. A first or second order regression equation may be used to fit to the data. No higher order of regression is allowed. The correlation coefficient must be >0.990. A plot of the calibration curve and standards must be supplied with the sample results.

5.2.1.1 Perform an Initial Calibration by injecting each of the five Calibration Standards and a hexane blank. To establish the RT window for the PCB congener peaks, use the mean of the absolute RT from the above chromatograms as the mid-point and ±3 times the standard deviation as calculated below for each congener.

5.2.1.2 Verify the retention time shift for the tetrachloro-m-xylene and/or decachlorobiphenyl in each analytical standard. The retention time shift between the initial and subsequent standards must be less than 0.3 percent. If this criterion is not met, continue injecting replicate standards to meet criteria.

5.2.1.3 Calculate the standard deviation of the five absolute retention times for each PCB congener in each CAL STD.

5.2.1.4 The standard deviations determined in Paragraph 5.2.1.3 shall be used to determine the retention time windows for a particular analytical sequence. Apply plus or minus three times the standard deviations in Paragraph 5.2.1.3 to the retention time of each PCB congener determined for the first analysis of the PCB standard in a given analytical analytical sequence. This range of retention times defines the retention time window for the compound of interest for that analytical sequence. The experience of the analyst should weigh heavily in the interpretation of chromatograms.

5.2.1.5 In those cases where the retention time window for a particular PCB congener is less than ±0.01 minutes, the laboratory may substitute whichever of the following formulae apply.

- For wide bore capillary columns (ID greater than 0.32 mm), the retention time window of the particular PCB congener shall be calculated as ±0.25% of the initial retention time of the compound in the analytical sequence.

- For narrow bore capillary columns (ID less than 0.32 mm), the retention time window of the particular PCB congener shall be calculated as ±0.15% of the initial retention time of the compound in the analytical sequence.

5.2.1.6 Regardless of whether the retention time windows are calculated by the method in Paragraph 5.2.2.4 or 5.2.2.5, the retention time windows must be reported as a range of values, not as, for example, 1.51 minutes ±1%.

5.2.1.7 The Laboratory must calculate retention time windows for each PCB congener on each GC column used at the beginning of the program and whenever a new GC column is installed. The data must be retained by the Laboratory and made available during an on-site laboratory evaluation.

5.3 Primary GC Column Analysis

5.3.1 Primary Analysis establishes whether or not PCB congeners are present in the sample, and establishes a tentative identification of each PCB congener. Quantitation may be performed on the primary analysis if the analysis meets all of the QC criteria specified for quantitation. **NOTE**: To determine that no PCB congeners are present at or above the method detection limit is a form of quantitation.

5.3.2 Calibration Standards

5.3.2.1 Prepare the Calibration Standards at the 5 concentration levels described in Section III. Analyze the five Calibration Standards sequentially at the beginning of each analytical sequence.

5.3.2.2 Calculate the Calibration Factor (ratio of the total area to the mass injected) for each PCB congener in each CAL STD using the following equation:

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}}{\text{Mass Injected (in nanograms)}}$$

5.3.2.3 Using the Calibration Factors from Paragraph 5.3.3.2 above, calculate the percent relative standard deviation (%RSD) for each compound at the five concentration levels using the following equation. The percent relative standard deviation for each compound must be ≤30.0 percent. The percent relative standard deviation for tetrachloro-m-xylene and/or decachlorobiphenyl must be ≤30.0 percent.

$$\%RSD = \frac{SD}{\overline{X}} \times 100$$

Where:

RSD = Relative Standard Deviation

SD = Standard Deviation of initial relative response factors (per compound)

Where:

$$SD = \sqrt{\frac{\sum_{i=1}^{N}\left(x_i - \overline{x_i}\right)^2}{N - 1}}$$

$\overline{x_i}$ = mean of initial relative response factors (per compound)

5.4 Sample Analysis (Primary GC Column)

5.4.1 Samples are analyzed per the sequence described in Table 8.

5.4.2 The retention time shift for the tetrachloro-m-xylene and/or decachlorobiphenyl surrogate standards must be evaluated after the analysis of each sample. The retention time shift may not exceed a 0.3% difference for capillary GC columns between the initial standard analysis and any sample analyzed during theanalytical sequence.

Calculate the percent difference in the retention time for each of the surrogate standards using the following equation:

$$\text{Percent Difference (\%D)} = \frac{RT_I - RT_S}{RT_I} \times 100$$

Where:

RT_I = absolute retention time of the surrogate standard in the initial standard (CAL STD-1).

RT_S = absolute retention time of the surrogate standard in the sample.

5.4.3 Evaluate the GC column throughout the analysis of samples by injecting CAL STD 3 at the frequency outlined in Table 8.

5.4.4 If one or more compounds have a response greater than CAL STD 5, the extract requires dilution according to the specifications in Section IV. If the dilution of the extract causes any compounds tentatively identified in the first analysis to be undetectable in the second analysis, then the results of both analyses shall be reported.

5.5 Confirmation Analysis (GC/ECD)

5.5.1 Confirmation Analysis is to confirm the identification and quantitation of all PCB congeners tentatively identified in the Primary Analysis.

5.5.2 Separation should be >25 percent resolution between peaks for BZ#28 and BZ#31. When this criteria cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

Calculate the percent resolution as follows:

$$\text{Percent Resolution} = \frac{H_v}{H_p} \times 100$$

Where:

H_v = the minimum height of the valley between the peaks

H_p = The maximum height of the peaks

5.5.3 All QC specified previously must be adhered to, i.e., linearity, calibration factor for standards, and retention time shift for the tetrachloro-m-xylene and/or decachlorobiphenyl surrogate standards.

5.5.4 Begin the Confirmation Analysis GC sequence with the five concentration levels of CAL STDs.

5.5.5 After the linearity standards required in 5.5.4 are injected, continue the confirmation analysis injection sequence with all compounds tentatively identified during primary analysis to establish the daily retention time windows during primary analysis. Analyze all confirmation standards for a case at the beginning, at intervals specified in 5.5.6 and at the end. Any PCB congener outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all samples between the standard that exceeds the criterion and a subsequent standard that meets the criterion. This reanalysis must be performed within the holding times specified in Section II, Paragraph 2.

5.5.6 Begin injection of samples at this point of the Confirmation Analysis sequence. Analyze groups of 5 samples with a CAL STD-3 after each group. The alternating CAL STD-3's calibration factors must be within 15.0 percent of each other if quantitation is performed. Deviations larger than 15.0 percent require the laboratory to repeat the samples analyzed following the standard that exceeds the criteria. The reanalysis must be performed within the holding times specified Section II, Paragraph 2. The 15.0 percent criteria only pertains to compounds being quantitated.

If the samples are split between 2 or more instruments, all appropriate standards and method blanks pertaining to those samples must be analyzed on each instrument.

5.5.7 Inject the method blank (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

5.5.8 If quantitation is performed on the confirmation analysis, follow the instructions in Paragraph 5.4.5 regarding dilution of extracts and reporting results.

SECTION V

TABLES

Table 1 - Numbering System For PCB Congeners(2)

BZ#	Structure	BZ#	Structure
-	Biphenyl	41	2,2',3,4-Tetrachlorobiphenyl
1	2-Chlorobiphenyl	42	2,2',3,4'-Tetrachlorobiphenyl
2	3-Chlorobiphenyl	43	2,2',3,5-Tetrachlorobiphenyl
3	4-Chlorobiphenyl	44	2,2',3,5'-Tetrachlorobiphenyl
4	2,2'-Dichlorobiphenyl	45	2,2',3,6-Tetrachlorobiphenyl
5	2,3-Dichlorobiphenyl	46	2,2',3,6'-Tetrachlorobiphenyl
6	2,3'-Dichlorobiphenyl	47	2,2',4,4'-Tetrachlorobiphenyl
7	2,4-Dichlorobiphenyl	48	2,2',4,5-Tetrachlorobiphenyl
8	2,4'-Dichlorobiphenyl	49	2,2',4,5'-Tetrachlorobiphenyl
9	2,5-Dichlorobiphenyl	50	2,2',4,6-Tetrachlorobiphenyl
10	2,6-Dichlorobiphenyl	51	2,2',4,6'-Tetrachlorobiphenyl
11	3,3'-Dichlorobiphenyl	52	2,2',5,5'-Tetrachlorobiphenyl
12	3,4-Dichlorobiphenyl	53	2,2',5,6'-Tetrachlorobiphenyl
13	3,4'-Dichlorobiphenyl	54	2,2',6,6'-Tetrachlorobiphenyl
14	3,5-Dichlorobiphenyl	55	2,3,3',4-Tetrachlorobiphenyl
15	4,4'-Dichlorobiphenyl	56	2,3,3',4'-Tetrachlorobiphenyl
16	2,2',3-Trichlorobiphenyl	57	2,3,3',5-Tetrachlorobiphenyl
17	2,2',4-Trichlorobiphenyl	58	2,3,3',5'-Tetrachlorobiphenyl
18	2,2',5-Trichlorobiphenyl	59	2,3,3',6-Tetrachlorobiphenyl
19	2,2',6-Trichlorobiphenyl	60	2,3,4,4'-Tetrachlorobiphenyl
20	2,3,3'-Trichlorobiphenyl	61	2,3,4,5-Tetrachlorobiphenyl
21	2,3,4-Trichlorobiphenyl	62	2,3,4,6-Tetrachlorobiphenyl
22	2,3,4'-Trichlorobiphenyl	63	2,3,4',5-Tetrachlorobiphenyl
23	2,3,5-Trichlorobiphenyl	64	2,3,4',6-Tetrachlorobiphenyl
24	2,3,6-Trichlorobiphenyl	65	2,3,5,6-Tetrachlorobiphenyl
25	2,3',4-Trichlorobiphenyl	66	2,3',4,4'-Tetrachlorobiphenyl
26	2,3',5-Trichlorbiphenyl	67	2,3',4,5-Tetrachlorobiphenyl
27	2,3',6-Trichlorobiphenyl	68	2,3',4,5'-Tetrachlorobiphenyl
28	2,4,4'-Trichlorobiphenyl	69	2,3',4,6-Tetrachlorobiphenyl
29	2,4,5-Trichlorobiphenyl	70	2,3',4',5-Tetrachlorobiphenyl
30	2,4,6-Trichlorobiphenyl	71	2,3',4',6-Tetrachlorobiphenyl
31	2,4',5-Trichlorobiphenyl	72	2,3',5,5'-Tetrachlorobiphenyl
32	2,4',6-Trichlorobiphenyl	73	2,3',5',6-Tetrachlorobiphenyl
33	2',3,4-Trichlorobiphenyl	74	2,4,4',5-Tetrachlorobiphenyl
34	2',3,5-Trichlorobiphenyl	75	2,4,4',6-Tetrachlorobiphenyl
35	3,3',4-Trichlorobiphenyl	76	2',3,4,5-Tetrachlorobiphenyl
36	3,3',5-Trichlorobiphenyl	77	3,3',4,4'-Tetrachlorobiphenyl
37	3,4,4'-Trichlorobiphenyl	78	3,3',4,5-Tetrachlorobiphenyl
38	3,4,5-Trichlorobiphenyl	79	3,3',4,5-Tetrachlorobiphenyl
39	3,4',5-Trichlorobiphenyl	80	3,3',5,5'-Tetrachlorobiphenyl
40	2,2',3,3'-Tetrachlorobiphenyl		

Table 1 - Numbering System For PCB Congeners(2) (Continued)

BZ#	Structure	BZ#	Structure
81	3,4,4',5-Tetrachlorobiphenyl	121	2,3',4,5',6-Pentachlorobiphenyl
82	2,2',3,3',4-Pentachlorobiphenyl	122	2',3,3',4,5-Pentachlorobiphenyl
83	2,2',3,3',5-Pentachlorobiphenyl	123	2',3,4,4',5-Pentachlorobiphenyl
84	2,2',3,3',6-Pentachlorobiphenyl	124	2',3,4,5,5'-Pentachlorobiphenyl
85	2,2',3,4,4'-Pentachlorobiphenyl	125	2',3,4,5,6'-Pentachlorobiphenyl
86	2,2',3,4,5-Pentachlorobiphenyl	126	3,3',4,4',5-Pentachlorobiphenyl
87	2,2',3,4,5'-Pentachlorobiphenyl	127	3,3',4,5,5'-Pentachlorobiphenyl
88	2,2',3,4,6-Pentachlorobiphenyl	128	2,2',3,3',4,4'-Hexachlorobiphenyl
89	2,2',3,4,6-Pentachlorobiphenyl	129	2,2',3,3',4,5-Hexachlorobiphenyl
90	2,2',3,4',5-Pentachlorobiphenyl	130	2,2',3,3',4,5'-Hexachlorobiphenyl
91	2,2',3,4',6-Pentachlorobiphenyl	131	2,2',3,3',4,6-Hexachlorobiphenyl
92	2,2',3,5,5'-Pentachlorobiphenyl	132	2,2',3,3',4,6'-Hexachlorobiphenyl
93	2,2',3,5,6-Pentachlorobiphenyl	133	2,2',3,3',5,5'-Hexachlorobiphenyl
94	2,2',3,5,6'-Pentachlorobiphenyl	134	2,2',3,3',5,6-Hexachlorobiphenyl
95	2,2',3,5',6-Pentachlorobiphenyl	135	2,2',3,3',5,6'-Hexachlorobiphenyl
96	2,2',3,6,6'-Pentachlorobiphenyl	136	2,2',3,3',6,6'-Hexachlorobiphenyl
97	2,2',3',4,5-Pentachlorobiphenyl	137	2,2',3,4,4',5-Hexachlorobiphenyl
98	2,2',3',4,6-Pentachlorobiphenyl	138	2,2',3,4,4',5'-Hexachlorobiphenyl
99	2,2',4,4',5-Pentachlorobiphenyl	139	2,2',3,4,4',6-Hexachlorobiphenyl
100	2,2',4,4',6-Pentachlorobiphenyl	140	2,2',3,4,4',6'-Hexachlorobiphenyl
101	2,2',4,5,5'-Pentachlorobiphenyl	141	2,2',3,4,5,5'-Hexachlorobiphenyl
102	2,2',4,5,6'-Pentachlorobiphenyl	142	2,2',3,4,5,6-Hexachlorobiphenyl
103	2,2',4,5',6-Pentachlorobiphenyl	143	2,2',3,4,5,6'-Hexachlorobiphenyl
104	2,2',4,6,6'-Pentachlorobiphenyl	144	2,2',3,4,5',6-Hexachlorobiphenyl
105	2,3,3',4,4'-Pentachlorobiphenyl	145	2,2',3,4,6,6'-Hexachlorobiphenyl
106	2,3,3',4,5-Pentachlorobiphenyl	146	2,2',3,4',5,5'-Hexachlorobiphenyl
107	2,3,3',4',5-Pentachlorobiphenyl	147	2,2',3,4',5,6-Hexachlorobiphenyl
108	2,3,3',4,5'-Pentachlorobiphenyl	148	2,2',3,4',5,6'-Hexachlorobiphenyl
109	2,3,3',4,6-Pentachlorobiphenyl	149	2,2',3,4',5',6-Hexachlorobiphenyl
110	2,3,3',4',6-Pentachlorobiphenyl	150	2,2',3,4',6,6'-Hexachlorobiphenyl
111	2,3,3',5,5'-Pentachlorobiphenyl	151	2,2',3,5,5',6-Hexachlorobiphenyl
112	2,3,3',5,6-Pentachlorobiphenyl	152	2,2',3,5,6,6'-Hexachlorobiphenyl
113	2,3,3',5',6-Pentachlorobiphenyl	153	2,2',4,4',5,5'-Hexachlorobiphenyl
114	2,3,4,4',5-Pentachlorobiphenyl	154	2,2',4,4',5,6'-Hexachlorobiphenyl
115	2,3,4,4',6-Pentachlorobiphenyl	155	2,2',4,4',6,6'-Hexachlorobiphenyl
116	2,3,4,5,6-Pentachlorobiphenyl	156	2,3,3',4,4',5-Hexachlorobiphenyl
117	2,3,4',5,6-Pentachlorobiphenyl	157	2,3,3',4,4',5'-Hexachlorobiphenyl
118	2,3',4,4',5-Pentachlorobiphenyl	158	2,3,3',4,4',6-Hexachlorobiphenyl
119	2,3',4,4',6-Pentachlorobiphenyl	159	2,3,3',4,5,5'-Hexachlorobiphenyl
120	2,3',4,5,5'-Pentachlorobiphenyl	160	2,3,3',4,5,6-Hexachlorobiphenyl

Table 1 - Numbering System For PCB Congeners(2) (Continued)

BZ#	Structure
161	2,3,3',4,5',6-Hexachlorobiphenyl
162	2,3,3',4',5,5'-Hexachlorobiphenyl
163	2,3,3',4',5,6-Hexachlorobiphenyl
164	2,3,3',4',5',6-Hexachlorobiphenyl
165	2,3,3',5,5',6-Hexachlorobiphenyl
166	2,3,4,4',5,6-Hexachlorobiphenyl
167	2,3',4,4',5,5'-Hexachlorobiphenyl
168	2,3',4,4',5',6-Hexachlorobiphenyl
169	3,3',4,4',5,5'-Hexachlorobiphenyl
170	2,2',3,3',4,4',5-Heptachlorobiphenyl
171	2,2',3,3',4,4',6-Heptachlorobiphenyl
172	2,2',3,3',4,5,5'-Heptachlorobiphenyl
173	2,2',3,3',4,5,6-Heptachlorobiphenyl
174	2,2',3,3',4,5,6'-Heptachlorobiphenyl
175	2,2',3,3',4,5',6-Heptachlorobiphenyl
176	2,2',3,3',4,6,6'-Heptachlorobiphenyl
177	2,2',3,3',4',5,6-Heptachlorobiphenyl
178	2,2',3,3',5,5',6-Heptachlorobiphenyl
179	2,2',3,3',5,6,6'-Heptachlorobiphenyl
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl
181	2,2',3,4,4',5,6-Heptachlorobiphenyl
182	2,2',3,4,4',5,6'-Heptachlorobiphenyl
183	2,2',3,4,4',5',6-Heptachlorobiphenyl
184	2,2',3,4,4',6,6'-Heptachlorobiphenyl
185	2,2',3,4,5,5',6-Heptachlorobiphenyl
186	2,2',3,4,5,6,6'-Heptachlorobiphenyl
187	2,2',3,4',5,5',6-Heptachlorobiphenyl
188	2,2',3,4',5,6,6'-Heptachlorobiphenyl
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl
190	2,3,3',4,4',5,6-Heptachlorobiphenyl
191	2,3,3',4,4',5',6-Heptachlorobiphenyl
192	2,3,3',4,5,5',6-Heptachlorobiphenyl
193	2,3,3',4',5,5',6-Heptachlorobiphenyl
194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl
196	2,2',3,3',4,4',5',6-Octachlorobiphenyl
197	2,2',3,3',4,4',6,6'-Octachlorobiphenyl
198	2,2',3,3',4,5,5',6-Octachlorobiphenyl
199	2,2',3,3',4,5,6,6'-Octachlorobiphenyl (IUPAC #200)
200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl (IUPAC #201)
201	2,2',3,3',4',5,5',6-Octachlorobiphenyl (IUPAC #199)
202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl
203	2,2',3,4,4',5,5',6-Octachlorobiphenyl
204	2,2',3,4,4',5,6,6'-Octachlorobiphenyl
205	2,3,3',4,4',5,5',6-Octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl
209	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl

Table 2. Surrogate Spiking Compounds

Compound	Theoretical Amount in Sample Extract* (before any optional dilutions)
Tetrachloro-m-xylene	0.2 µg
AND/OR	
Decachlorobiphenyl	0.2 µg

* At the time of injection assuming 100% extraction efficiency.

Table 3 - PCB Congener Matrix Spiking Solution

Congener	Concentration (µg/mL)
2,4'-Dichlorobiphenyl	0.2
2,2',5-Trichlorobipheny	0.2
2,4,4'-Trichlorobiphenyl	0.2
2,2',3,5'-Tetrachlorobiphenyl	0.2
2,2',5,5'-Tetrachlorobiphenyl	0.2
2,3',4,4'-Tetrachlorobiphenyl	0.2
3,3',4,4'-Tetrachlorobiphenyl	0.2
2,2',4,5,5'-Pentachlorobiphenyl	0.2
2,3,3',4,4'-Pentachlorobiphenyl	0.2
2,3',4,4',5-Pentachlorobiphenyl	0.2
3,3',4,4',5-Pentachlorobiphenyl	0.2
2,2',3,3',4,4'-Hexachlorobiphenyl	0.2
2,2',3,4,4',5'-Hexachlorobiphenyl	0.2
2,2',4,4',5,5'-Hexachlorobiphenyl	0.2
2,2',3,3',4,4',5-Heptachlorobiphenyl	0.2
2,2',3,4,4',5,5'-Heptachlorobiphenyl	0.2
2,2',3,4',5,5',6-Heptachlorobiphenyl	0.2
2,2',3,3',4,4',5,6-Octachlorobiphenyl	0.2
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	0.2
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	0.2

Table 4 - PCB Congeners for Calibration Standards

BZ#	Structure	BZ#	Structure
1	2-Chlorobiphenyl	105	2,3,3',4,4'-Pentachlorobiphenyl
3	4-Chlorobiphenyl	107	2,3,3',4',5-Pentachlorobiphenyl
4	2,2'-Dichlorobiphenyl	115	2,3,4,4',6-Pentachlorobiphenyl
5	2,3-Dichlorobiphenyl	119	2,3',4,4',6-Pentachlorobiphenyl
6	2,3'-Dichlorobiphenyl	122	2',3,3',4,5-Pentachlorobiphenyl
9	2,5-Dichlorobiphenyl	123	2',3,4,4',5-Pentachlorobiphenyl
12	3,4-Dichlorobiphenyl	128	2,2',3,3',4,4'-Hexachlorobiphenyl
15	4,4'-Dichlorobiphenyl	129	2,2',3,3',4,5-Hexachlorobiphenyl
16	2,2',3-Trichlorobiphenyl	136	2,2',3,3',6,6'-Hexachlorobiphenyl
18	2,2',5-Trichlorobiphenyl	137	2,2',3,4,4',5-Hexachlorobiphenyl
19	2,2',6-Trichlorobiphenyl	138	2,2',3,4,4',5'-Hexachlorobiphenyl
22	2,3,4'-Trichlorobiphenyl	141	2,2',3,4,5,5'-Hexachlorobiphenyl
25	2,3',4-Trichlorobiphenyl	149	2,2',3,4',5',6-Hexachlorobiphenyl
26	2,3',5-Trichlorbiphenyl	151	2,2',3,5,5',6-Hexachlorobiphenyl
27	2,3',6-Trichlorobiphenyl	153	2,2',4,4',5,5'-Hexachlorobiphenyl
28	2,4,4'-Trichlorobiphenyl	157	2,3,3',4,4',5'-Hexachlorobiphenyl
29	2,4,5-Trichlorobiphenyl	158	2,3,3',4,4',6-Hexachlorobiphenyl
31	2,4',5-Trichlorobiphenyl	167	2,3',4,4',5,5'-Hexachlorobiphenyl
37	3,4,4'-Trichlorobiphenyl	170	2,2',3,3',4,4',5-Heptachlorobiphenyl
40	2,2',3,3'-Tetrachlorobiphenyl	171	2,2',3,3',4,4',6-Heptachlorobiphenyl
41	2,2',3,4-Tetrachlorobiphenyl	177	2,2',3,3',4',5,6-Heptachlorobiphenyl
44	2,2',3,5'-Tetrachlorobiphenyl	180	2,2',3,4,4',5,5'-Heptachlorobiphenyl
47	2,2',4,4'-Tetrachlorobiphenyl	183	2,2',3,4,4',5',6-Heptachlorobiphenyl
49	2,2',4,5'-Tetrachlorobiphenyl	185	2,2',3,4,5,5',6-Heptachlorobiphenyl
52	2,2',5,5'-Tetrachlorobiphenyl	187	2,2',3,4',5,5',6-Heptachlorobiphenyl
53	2,2',5,6'-Tetrachlorobiphenyl	189	2,3,3',4,4',5,5'-Heptachlorobiphenyl
56	2,3,3',4'-Tetrachlorobiphenyl	190	2,3,3',4,4',5,6-Heptachlorobiphenyl
66	2,3,4,4'-Tetrachlorobiphenyl	191	2,3,3',4,4',5',6-Heptachlorobiphenyl
70	2,3',4',5-Tetrachlorobiphenyl	193	2,3,3',4',5,5',6-Heptachlorobiphenyl
75	2,4,4',6-Tetrachlorobiphenyl	194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
77	3,3',4,4'-Tetrachlorobiphenyl	195	2,2',3,3',4,4',5,6-Octachlorobiphenyl
82	2,2',3,3',4-Pentachlorobiphenyl	196	2,2',3,3',4,4',5',6-Octachlorobiphenyl
83	2,2',3,3',5-Pentachlorobiphenyl	198	2,2',3,3',4,5,5',6-Octachlorobiphenyl
84	2,2',3,3',6-Pentachlorobiphenyl	199	2,2',3,3',4,5,6,6'-Octachlorobiphenyl
85	2,2',3,4,4'-Pentachlorobiphenyl	200	2,2',3,3',4,5',6,6'-Octachlorobiphenyl
87	2,2',3,4,5'-Pentachlorobiphenyl	201	2,2',3,3',4',5,5',6-Octachlorobiphenyl
91	2,2',3,4',6-Pentachlorobiphenyl	202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl
92	2,2',3,5,5'-Pentachlorobiphenyl	205	2,3,3',4,4',5,5',6-Octachlorobiphenyl
95	2,2',3,5',6-Pentachlorobiphenyl	206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
97	2,2',3',4,5-Pentachlorobiphenyl	207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
99	2,2',4,4',5-Pentachlorobiphenyl	208	2,2',3,3',4,,5,5',6,6'-Nonachlorobiphenyl
101	2,2',4,5,5'-Pentachlorobiphenyl		

Table 5

Capillary column 1 conditions: 40 m x 0.18 mm ID, 0.4 micron film thickness, fused silica DB-5 (or equivalent) splitless mode

Helium carrier gas:	ca 0.7 mL/min at 280°C and 25 PSI
95% Argon/5% Methane makeup gas:	30 mL/min
Septum purge:	15 mL/min
Split vent:	None
Initial temperature:	90°C, initial hold - 2 min
Temperature program 1:	10°C/min for 6 minutes
Temperature program 2:	3°C/min to 290°C.
Final temperature:	290°C, (Total Run 95 min)
Injection port temp.:	210°C
Detector temp.	300°C

Capillary column 2 conditions: 60 m x 0.25 mm ID, 0.25 micron film thickness, fused silica SP-2100, splitless mode

Helium carrier gas:	ca 0.7 mL/min at 280°C and 25 PSI
95% Argon/5% Methane makeup gas:	30 mL/min
Septum purge:	15 mL/min
Split vent:	None
Initial temperature:	150°C, initial hold - 5 min.
Temperature program 1:	15°C/min to 180°C - hold for 1 min.
Temperature program 2:	2°C/min. to 190°C
Final temperature:	190°C, (Total Run 85 min)
Injection port temp.:	200°C
Detector temperature	300°C

Table 6 - Relative Retention Times for Column 1

BZ #	RRT*	BZ #	RRT*	BZ #	RRT*
1	0.7968	67	1.7840	138	2.4866
2	0.8532	63	1.8021	158	2.5043
3	0.9096	74	1.8214	126,129	2.5241
10,4	0.9700	70	1.8337	187	2.5850
Surrogate	1.0000	66	1.8487	128	2.6037
7,9	1.0545	95	1.8540	183	2.6096
6	1.0850	91	1.8818	167	2.6316
8,5	1.1048	56,60	1.9187	185	2.6610
Hexachlorobenzene	1.1230	92,84	1.9439	174	2.6877
19	1.1717	90,101	1.9658	177	2.7091
12	1.2465	99	1.9888	156,171	2.7310
18	1.2551	119	2.0209	202	2.7465
15,17	1.2652	83	2.0332	201	2.7829
24,27	1.2952	97	2.0572	157.172.197	2.7952
16,32	1.3241	87	2.0770	180	2.8262
29	1.3882	115 + DDE	2.0882	193	2.8417
26	1.3979	85	2.0957	191	2.8620
25	1.4086	136	2.1107	200	2.8882
31	1.4278	77,110	2.1225	170	2.9524
28	1.4348	82	2.1684	190	2.9690
20,33,53	1.4733	151	2.1957	Mirex	2.9797
22	1.4984	135	2.2112	198	3.0080
45	1.5235	107	2.2257	199	3.0182
51	1.5529	123	2.2374	196,203	3.0460
52	1.5765	118,149	2.2492	189	3.1021
49	1.5963	146	2.2957	195	3.1754
47	1.6096	122	2.3096	208	3.1914
48,75	1.6171	105	2.3615	207	3.2289
44	1.6594	132,153	2.3684	194	3.2786
37,42,59	1.6743	141,179	2.4235	205	3.3128
41,64	1.7123	130	2.4342	206	3.4770
40	1.7433	137	2.4524		

* Relative Retention Times to surrogate compound tetrachloro-m-xylene

Table 7 - Relative Retention Times for Column 2

BZ #	RRT*	BZ #	RRT*	BZ #	RRT*
1	0.8018	63	1.7934	138	2.4723
3	0.9141	74	1.8134	158	2.4876
10,4	0.9736	70	1.8266	126,129	2.5076
Surrogate	1.0000	66	1.8419	187	2.5688
7,9	1.0543	95	1.8466	128	2.5867
6	1.0854	91	1.8730	183	2.5925
8,5	1.1060	56,60	1.9093	167	2.6136
Hexachlorobenzene	1.1244	92,84	1.9346	185	2.6431
19	1.1713	90,101	1.9568	174	2.6705
12	1.2441	99	1.9794	177	2.6911
18	1.2599	119	2.0095	156,171	2.7127
15,17	1.2625	83	2.0221	202	2.7285
24,27	1.2926	97	2.0469	201	2.7644
16,32	1.3221	87	2.0659	157.172.197	2.7760
29	1.3843	115 + DDE	2.0770	180	2.8076
26	1.3943	85	2.0843	193	2.8213
25	1.4038	136	2.1002	191	2.8413
31	1.4249	77,110	2.1118	200	2.8682
28	1.4312	82	2.1566	170	2.9320
20,33,53	1.4697	151	2.1834	190	2.9478
22	1.4939	135	2.1993	Mirex	2.9573
45	1.5187	107	2.2124	198	2.9868
51	1.5477	123	2.2246	199	2.9974
52	1.5720	118,149	2.2372	196,203	3.0242
49	1.5909	146	2.2826	189	3.0796
47	1.6036	122	2.2941	195	3.1523
48,75	1.6115	105	2.3463	208	3.1687
44	1.6537	132,153	2.3548	207	3.2056
37,42,59	1.6679	141,179	2.4085	194	3.2551
41,64	1.7059	130	2.4196	205	3.2889
40	1.7359	137	2.4365	206	3.4528
67	1.7765				

* Relative Retention Times to surrogate compound tetrachloro-m-xylene

Table 8 - Analytical Sequence for PCB Analysis:

1. CAL STD-1
2. CAL STD-2
3. CAL STD-3
4. CAL STD-4
5. CAL STD-5
6. Hexane Blank
7. 5 samples
8. CAL STD-3
9. Hexane Blank
10. 5 samples
11. Repeat the above sequence starting with CAL STD-3 (step 8 above). Continue as long as quality control requirements are met and no significant adjustments are made to the analytical system.
12. PCB analysis sequence must end end with the analyses of CAL STD-3

SECTION VI

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Exhibit E

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Part I -- Introduction

The quality assurance/quality control (QA/QC) procedures defined below must be used by the Laboratory when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibit D, the Laboratory must also follow these procedures. The cost of performing all QA/QC procedures specified in this Protocol is included in the per sample price of the contract. The cost of analyzing any NYSDEC submitted QA/QC samples (matrix spikes, matrix spike duplicates, matrix spike blanks, duplicates, spikes, laboratory control samples, trip blanks and blind QCs) will be billable as separate sample analysis.

The purpose of this document is to provide a uniform set of procedures for the analysis of organic and inorganic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The prime function of the QA/QC program outlined here is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any organic or inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation (Exhibit D). Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Laboratory must participate in the Laboratory Audit Program accepted by NYSDEC. The Laboratory can expect to analyze two sets of samples per twelve-month period for this program.

For QA/QC procedures, two different types of "samples" are specified. A "sample received" is the field or PE sample each of which has a NYSDEC sample number and is accompanied by a Contract Lab Sample Information Sheet. An "analytical sample" is each "analysis" performed (i.e. each cuvette, cup, tube or container in autosamplers, etc.). A "frequency of 10%" means once every 10 analytical samples.

***NOTE**: Calibration blanks and calibration verification samples are not counted as analytical samples when determining 10% frequency.*

If any QC measurement fails to meet protocol criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in Exhibit E.

The Laboratory must report all QC data in the exact format specified in Exhibits B and H.

The scope of the program is for all laboratory operations (from sample receipt, through analysis, to data reduction/reporting). The scope includes those audit procedures used to evaluate the application of the procedures defined within this QA/QC program.

Standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases should also be adhered to. For additional guidelines regarding these general laboratory procedures, please see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979. and 40CFR Part 792 on Good Laboratory Practice Standards.

Part II -- General QA/QC Considerations

Section I -- Introduction

Appropriate use of data generated under the large range of analytical conditions encountered in environmental analyses requires reliance on the quality control procedures and criteria incorporated into the methods. The methods in this Protocol have been validated on samples under various programs. However the validation of these methods does not guarantee that they perform equally well for all sample matrices encountered. Inaccuracies can also result from causes other than unanticipated matrix effects, such as sampling artifacts, equipment malfunctions, and operator error. Therefore, the quality control component of each method is indispensable.

The data acquired from quality control procedures are used to estimate and evaluate the information content of analytical results and to determine the necessity for or the effect of corrective action procedures. The parameters used to estimate information content include precision, accuracy, detection limit, and other quantitative and qualitative indicators. In addition, it gives an overview of the activities required in an integrated program to generate data of known and documented quality required to meet defined objectives.

The necessary components of a complete QA/QC program include internal QC criteria that demonstrate acceptable levels of performance, as determined by QA review. External review of data and procedures is accomplished by the monitoring activities of the Bureau of Watershed Assessment and Research (BWAR) and other NYSDEC Central Office Bureaus, Regional data users, and other data users and validators. Each external review accomplishes a different purpose. These reviews are described in specific sections of this Exhibit. Laboratory evaluation samples, magnetic tape audits, and data package audits provide an external QA reference for the program. A laboratory on-site evaluation system is also part of the external QA monitoring. A feedback loop provides the results of the various review functions to the Laboratories through direct communications with the BWAR and the Project Officers.

This Exhibit is not a guide to constructing quality assurance project plans, quality control systems, or a quality assurance organization. It is, however, an explanation of the quality control and quality assurance requirements of the program. It outlines some minimum standards for QA/QC programs. It also includes specific items that are required in a QA Program Plan and by the QA/QC documentation detailed in this Protocol. Delivery of this documentation provides the NYSDEC with a complete data package which will stand alone, and limits the need for contact with the Laboratory or with an analyst, at a later date, if some aspect of the analysis is questioned.

In order to assure that the product delivered by the Laboratory meets the requirements of the Protocol, and to improve interlaboratory data comparison, the NYSDEC requires the following from the Laboratory:

- A written Quality Assurance Plan, the elements of which are designated in Section II.

- Written preparation of and adherence to QA/QC Standard Operating Procedures (SOPs) as described in Section III.

- Adherence to the analytical methods and associated QC requirements specified in the Protocol.

- Verification of analytical standard and documentation of the purity of neat materials and the purity and accuracy of solutions obtained from private chemical supply houses.

- Submission of all raw data and pertinent documentation for Regional review.

- Participation in the analysis of Laboratory Evaluation Samples, including adherence to corrective action procedures.

- Submission, upon request, of GC/MS tapes and applicable documentation for tape audits.

- Participation in On-Site Laboratory Evaluations, including adherence to corrective action procedures.

- Submission of all original documentation generated during sample analyses for NYSDEC review.

1. QA/QC Standard Operating Procedure (SOP)

The Laboratory shall have a written QA/QC Standard Operating Procedure (SOP) which describes the in-house procedures employed to guarantee, to the extent possible, the quality of all analysis activities. It should describe the quality assurance and the quality control procedures used during the analysis. Each Laboratory should prepare individual SOPs to suit the needs of that organization as has been best determined. A QA/QC SOP should contain essential elements described in this section.

2. Elements of a QA/QC SOP

2.1 All routine laboratory tasks should have written QA/QC Standard Operating Procedures. Standard Operating Procedures should be detailed documents describing who does what, when, where, how, and why. They should be sufficiently complete and detailed to ensure:

2.1.1 Data of known quality and integrity are generated.

2.1.2 The loss of data due to out-of-control conditions is minimized.

2.2 Standard Operating Procedures shall be:

2.2.1 Adequate to establish the traceability of standards, instrumentation, samples, and environmental data.

2.2.2 Simple, so a user with basic education, experience and/or training can properly use them.

2.2.3 Complete enough so the user follows the directions in a stepwise manner.

2.2.4 Consistent with sound scientific principles and good laboratory practices.

2.2.5 Consistent with current NYSDEC and USEPA regulations, guidelines, and Protocol requirements.

2.2.6 Consistent with the instrument manufacturer's specific instruction manuals.

2.3 Standard Operating Procedures shall also provide for documentation sufficiently complete to:

2.3.1 Record the performance of all tasks and their results.

2.3.2 Explain the cause of missing data.

2.3.4 Demonstrate the validation of data each time they are recorded, calculated, or transcribed.

2.3.5 Detail all standard preparations.

2.4 To accomplish these objectives, Standard Operating Procedures should address the major elements upon which the final quality of the Laboratory's work depends. In the following descriptions these six major areas have been divided into subelements, where applicable. These elements include, but are not limited to:

2.4.1 Organization and personnel,

2.4.2 Facilities and equipment,

2.4.3 Analytical methodology,

2.4.4 Sample custody procedures,

2.4.5 Quality control, and

2.4.6 Data handling.

3. Organization and Personnel

3.1 QA Policy and Objectives - Each organization should have a written quality assurance policy that should be made known to all organization personnel. Objectives should be established to produce data that meet Protocol requirements in terms of completeness, precision, accuracy, representativeness, documentation, and comparability. The SOP should require the preparation of a specific QA plan for the analysis.

3.2 QA Organization - The organization and management of the QA function should be described in the Laboratory's SOP. Reporting relationships and responsibilities should be clearly defined. A QA Coordinator or Supervisor should be appointed and his or her responsibilities established. A description of the QC paperwork flow should be available. There should be a clear designation of those who are authorized to approve data and results. Responsibilities for taking corrective action should be assigned to appropriate management personnel.

3.3 Personnel training - The Laboratory shall incorporate a training program for all new employees. this program shall be documented in the employee personnel folder. This system should include motivation toward producing data of acceptable quality and should involve "practice work" by the new employee. The quality of this work can be immediately verified and discussed by the supervisor, with appropriate corrective action taken.

3.4 Document Control and Revisions - The SOP should include a system for documenting:

3.4.1 Calibration procedures,

3.4.2 Analytical procedures,

3.4.3 Computational procedures,

3.4.4 Quality control procedures,

3.4.5 Bench data,

3.4.6 Operating procedures, or any changes to these procedures, and

3.4.7 Laboratory notebook policy.

3.5 Procedures for making revisions to technical procedure or documents must be clearly defined, with the lines of authority indicated. Procedural revisions should be written and distributed to all affected individuals, thus ensuring implementation of changes.

4. Facilities and Equipment

4.1 Procurement and Inventory Procedures - Purchasing guidelines for all equipment and reagents having an effect on data quality should be well-defined and documented. Similarly, performance specifications should be documented for all items of equipment having an effect on data quality. Once any item which is critical to the analysis such as an in situ instrument, or reagent is received and accepted by the organization, documentation should be retained of the type, age, and acceptance status of the item. Reagents should be dated upon receipt in order to establish their order of use and to minimize the possibility of exceeding their useful shelf life.

4.2 Preventive Maintenance - Preventive maintenance procedures should be clearly defined and written for each measurement system and required support equipment. When maintenance activity is necessary, it should be documented on standard forms maintained in logbooks. A history of the maintenance record of each system serves as an indication of the adequacy of maintenance schedules and parts inventory.

5. Analytical Methodology

5.1 Calibration and Operating Procedures - Calibration is the process of establishing the relationship of a measurement system output to a known stimulus. In

essence, calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration SOP should include provisions for documentation of frequency, conditions, standards, and records reflecting the calibration history of a measurement system.

5.1.1 The accuracy of the calibration standards is an important point to consider since all data will be in reference to the standards used. An SOP for verifying the accuracy of all working standards against primary grade standards should be routinely followed.

5.2 Feedback and corrective action - The SOP should specify the corrective action that is to be taken when an analytical or sampling error is discovered or the analytical system is determined to be out of control. The SOP should require documentation of the corrective action and notification of the analyst of the error and correct procedures.

6. Sample Custody

6.1 Sample custody is a part of any good laboratory or field operation. Where samples may be needed for legal purposes, "chain-of-custody" procedures, as defined in Exhibit F must be used. However, at a minimum, the following sample custody procedures should be addressed in the QA/QC SOP.

6.2 Chain-of-Custody in laboratory operations

6.2.1 Identification of responsible party to act as sample custodian at the laboratory facility authorized to sign for incoming field samples, obtain documents of shipment (e.g., bill of lading number or mail receipt), and verify the data entered onto the sample custody records.

6.2.2 Provision for a laboratory sample custody log consisting of serially numbered standard lab-tracking report sheets.

6.2.3 Specification of laboratory sample custody procedures for sample handling, storage and dispersement for analysis.

7. Quality Control

7.1 Quality Control Procedures - The quality control procedures used during analysis should be described and must conform to those described in Exhibit E. The quality control checks routinely performed during sample analysis include method blank analysis to establish analyte levels, duplicate analysis to establish analytical precision, spiked and blank sample analysis to determine analytical accuracy, and 40CFR Part 792 on Good Laboratory Practice Standards. The frequency of these quality assurance checks are defined in the Protocol. Limits of acceptance or rejection are also defined for analysis and control charts should be used. Confirmation procedures should be described in the SOP.

7.2 Control Checks and Internal Audits - A good SOP will make provision for and describe control checks and internal audits by the Laboratory. Several approaches are used for control checks. These include:

7.2.1 Reference material analysis. Analytical reference materials are available from several commercial and government sources, or they may be prepared in-house. The chemical analysis of these materials has been well established. Such materials can be analyzed along side routine samples and the results used to check the accuracy of analytical procedures. All reference materials must be free from contaminates.

7.2.2 Blank analysis. The procedures and the frequency of blank analyses are defined in the Protocol.

7.2.3 Matrix spike, matrix spike duplicate, and matrix spike blank analysis. The procedures and the frequency of matrix spike analyses are defined in the Protocol.

7.2.4 Duplicate analysis. The procedures and the frequency of duplicate analyses are defined in the Protocol.

7.2.5 Internal audits. Internal audits should be periodically conducted to evaluate the functioning of the QA SOP. This involves an independent check of the performance of the Laboratory analysts to determine if prescribed procedures are closely followed. Reports of internal audits performed in connection with this Protocol shall be available for inspection during the on-site audit performed under the direction of NYSDEC.

8. Data Handling

8.1 Data Handling, Reporting and Recordkeeping - Data handling, reporting, and recordkeeping procedures should be described. Data handling and reporting includes all procedures used to record data on standard forms, and in laboratory notebooks. The reporting format for different types of bench data should be described and the forms provided. The contents of notebooks should be specified.

8.1.1 Recordkeeping of this type serves at least two useful functions:

8.1.1.1 it makes possible the reanalysis of a set of data at a future time, and

8.1.1.2 it may be used in support of the experimental conclusions if various aspects of the analysis are called into question.

8.2 Data Reduction - Data reduction procedures, defined ideally as a set of computerized and manual checks applied at various appropriate levels of the measurement process, should be in written form and clearly defined for all measurement systems.

8.2.1 Criteria for data reduction must be documented and include limits on:

8.2.1.1 Operational parameters such as GC conditions

8.2.1.2 Calibration data

8.2.1.3 Special checks unique to each measurement, e.g., successive values/averages

8.2.1.4 Statistical tests, e.g., outliers

8.2.1.5 Manual checks such as hand calculations.

8.2.2 The limits defined in the protocol ensure a high probability of detecting invalid data for either all or the majority of the measurement systems. The required data reduction activities (GC operating conditions, analytical precision, etc.) should be recorded on standard forms in a logbook.

Section II -- Quality Assurance Program Plan

The Laboratory shall establish a quality assurance program with the objective of providing sound analytical chemical measurements. This program shall incorporate the quality control procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production.

As evidence of such a program, the Laboratory shall prepare a written Quality Assurance Program Plan (QAPP) which describes the procedures that are implemented to achieve the following:

- Maintain data integrity, validity, and usability.
- Ensure that analytical measurement systems are maintained in an acceptable state of stability and reproducibility .
- Detect problems through data assessment and establishes corrective action procedures which keep the analytical process reliable.
- Document all aspects of the measurement process in order to provide data which are technically sound and legally defensible.

The QAPP must present, in specific terms, the policies, organization, objectives, functional guidelines, and specific QA and QC activities designed to achieve the data quality requirements in this Protocol. Where applicable, SOPs pertaining to each element shall be included or referenced as part of the QAPP. The QAPP must be available during On-Site Laboratory evaluation. Additional information relevant to the preparation of a QAPP can be found in EPA and ASTM publications.

Elements of a Quality Assurance Plan

1. Organization and Personnel

1.1 QA Policy and Objectives

1.2 QA Management

1.2.1 Organization

1.2.2 Assignment of QC and QA Responsibilities

1.2.3 Reporting Relationships

1.2.4 QA Document Control Procedures

1.2.5 QA Program Assessment Procedures

1.3 Personnel

1.3.1 Resumes

1.3.2 Education and Experience Pertinent to This Protocol

1.3.3 Training Progress

2. Facilities and Equipment

2.1 Instrumentation and Backup Alternatives

2.2 Maintenance Activities and Schedules

2.3 Waste Disposal Facilities

3. Document Control

3.1 Laboratory Notebook Policy

3.2 Samples Tracking/Custody Procedures

3.3 Logbook Maintenance and Archiving Procedures

3.4 Case File Organization, Preparation and Review Procedures.

3.5 Procedures for Preparation, Approval, Review, Revision, and Distribution of SOPs.

3.6 Process for Revision of Technical or Documentation Procedures

4. Analytical Methodology

4.1 Calibration Procedures and Frequency

4.2 Sample Preparation/Extraction Procedures

4.3 Sample Analysis Procedures

4.4 Standards Preparation Procedures

4.5 Decision Processes, Procedures, and Responsibility for Initiation of Corrective Action

5. Data Generation

5.1 Data Collection Procedures

5.2 Data Reduction Procedures

5.3 Data Validation Procedures

5.4 Data Reporting and Authorization Procedures

6. Quality Control

6.1 Solvent, Reagent and Adsorbent Check Analysis

6.2 Reference Material Analysis

6.3 Internal Quality Control Checks

6.4 Corrective Action and Determination of QC Limit Procedures

6.5 Responsibility Designation

7. Quality Assurance

7.1 Documentation of Appropriate Laboratory Certifications

7.2 Data Quality Assurance

7.3 Systems/Internal Audits

7.4 Performance/External Audits

7.5 Corrective Action Procedures

7.6 Quality Assurance Reporting Procedures

7.7 Responsibility Designation

Updating and Submission of the QAPP:

Within 60 Days of contract award:

During the contract solicitation process, the Laboratory was required to submit their QAPP to BWAR. Within sixty (60) days after contract award, the Laboratory shall send a revised QAPP, fully compliant with the requirements of this Protocol, to the BWAR. The revised QAPP will become the official QAPP under this Protocol. The revised QAPP must include:

1) Changes resulting from:

   A) The Laboratory's internal review of their organization, personnel, facility, equipment, policy and procedures and

   B) The Laboratory's implementation of the requirements of the Protocol; and,

2) Changes resulting from the NYSDEC's review of the laboratory evaluation sample data, bidder supplied documentation, and recommendations made during the pre-award On-Site laboratory evaluation.

Subsequent submissions:

During the term of contract, the Laboratory shall amend the QAPP when the following circumstances occur:

1) The NYSDEC modifies the contract,

2) The NYSDEC notifies the Laboratory of deficiencies in the QAPP document

3) The NYSDEC notifies the Laboratory of deficiencies resulting from the NYSDEC's review of the Laboratory's performance,

4) The Laboratory identifies deficiencies resulting from their internal review of their QAPP document,

5) The Laboratory's organization, personnel, facility, equipment, policy or procedures change,

6) The Laboratory identifies deficiencies resulting from the internal review of their organization, personnel, facility, equipment, policy or procedures changes.

The Laboratory shall amend the QAPP within 30 days of when the circumstances listed above result in a discrepancy between what was previously described in the QAPP and what is presently occurring at the Laboratory's facility.

When the QAPP is amended, all changes in the QAPP must be clearly marked (e.g., a bar in the margin indicating where the change is found in the document, or highlighting the change by underlining the change, bold printing the change, or using a different print font). The amended section pages must have the date on which the changes were implemented. The Laboratory shall incorporate all amendments to the current QAPP document. The Laboratory shall archive all amendments to the QAPP document for future reference by the NYSDEC.

The Laboratory shall send a copy of the current QAPP document within 14 days of a request by the Bureau of Program Services and Research to the designated recipients.

Corrective Action:

If a Laboratory fails to adhere to the requirements listed in Section II, a Laboratory may expect, but the NYSDEC is not limited to the following actions: reduction of numbers of samples sent under this contract, suspension of sample shipment to the Laboratory, GC/MS tape audit, data package audit, an On-Site laboratory evaluation , remedial laboratory evaluation sample, and/or contract sanctions, such as a Cure Notice.

Section III -- Standard Operating Procedures (SOPs)

In order to obtain reliable results, adherence to prescribed analytical methodology is imperative. In any operation that is performed on a repetitive basis, reproducibility is best accomplished through the use of Standard Operating Procedures (SOPs). As defined by the NYSDEC, an SOP is a written document which provides directions for the step-by-step execution of an operation, analysis, or action which is commonly accepted as the method for performing certain routine or repetitive tasks.

SOPs prepared by the Laboratory must be functional: i.e., clear, comprehensive, up-to-date, and sufficiently detailed to permit duplication of results by qualified analysts. All SOPs, as presented to the NYSDEC, must reflect activities as they are currently performed in the Laboratory. Photocopies of published methods are not acceptable SOPs by themselves. In addition, all SOPs must be:

- Consistent with current EPA and NYSDEC regulations, guidelines, and the Analytical Services Protocol's requirements.
- Consistent with instruments manufacturer's specific instruction manuals.
- Available to the NYSDEC during an On-Site Laboratory Evaluation. A complete set of SOPs shall be bound together and available for inspection at such evaluations. During On-Site Laboratory evaluations, laboratory personnel may be asked to demonstrate the application of the SOPs.
- Capable of providing for the development of documentation that is sufficiently complete to record the performance of all tasks required by the Protocol.
- Capable of demonstrating the validity of data reported by the Laboratory and explain the cause of missing or inconsistent results.
- Capable of describing the corrective measures and feedback mechanism utilized when analytical results do not meet Protocol requirements.
- Reviewed regularly and updated as necessary when contract, facility, or Laboratory procedural modifications are made.
- Archived for future reference in usability or evidentiary situations.
- Available at specific work stations as appropriate
- Subject to a document control procedure which precludes the use of outdated or inappropriate SOPs.

SOP FORMAT:

The format for SOPs may vary depending upon the kind of activity for which they are prepared, however, at a minimum, the following sections must be included:

- Title Page
- Scope and Application

- Definitions
- Procedures
- QC Limits
- Corrective Action Procedures, Including Procedures for Secondary Review of Information Being Generated
- Documentation Description and Example Forms
- Miscellaneous Notes and Precautions
- References

SOPS REQUIRED:

The following SOPs are required by the NYSDEC:

1. Evidentiary SOP

Evidentiary SOPs for required chain-of-custody and document control are discussed in Exhibit F, "Specification for Written Standard Operating Procedures"

2. Sample Receipt and Storage

2.1 Sample receipt and identification logbooks

2.2 Refrigerator temperature logbooks

2.3 Extract storage logbooks

2.4 Security precautions

2.5 Waste Disposal

3. Sample Preparation

3.1 Reagent purity check procedures and documentation

3.2 Extraction procedures

3.3 Extraction bench sheets

3.4 Extraction logbook maintenance

4. Glassware Cleaning

5. Calibration (Balances, GPC)

5.1 Procedures

5.2 Frequency requirements

5.3 Preventative maintenance schedule and procedures

5.4 Acceptance criteria and corrective actions

5.5 Logbook maintenance authorization

6. Analytical Procedures (for each analytical system)

6.1 Instrument performance specifications

6.2 Instrument operating procedures

6.3 Data acquisition system operation

6.4 Procedures when automatic quantitation algorithms are overridden

6.5 QC required parameters

6.6 Analytical run/injection logbooks

6.7 Instrument error and editing flag descriptions and resulting corrective actions

7. Maintenance Activities (for each analytical system)

7.1 Preventative maintenance schedule and procedures

7.2 Corrective maintenance determinants and procedures

7.3 Maintenance authorization

8. Analytical Standards

8.1 Standard coding/identification and inventory system

8.2 Standards preparation logbook(s)

8.3 Standard preparation procedures

8.4 Procedures for equivalency/traceability analyses and documentation

8.5 Purity logbook (primary standards and solvents)

8.6 Storage, replacement, and labeling requirements

8.7 QC and corrective action measures

9. Data reduction Procedures

9.1 Data processing systems operation

9.2 Outlier identification methods

9.3 Identification of data requiring corrective action

9.4 Procedures for format and/or forms for each operation

10. Documentation Policy/Procedures

10.1 Laboratory/analyst's notebook policy, including review policy

10.2 Complete SDG File contents

10.3 Complete SDG File organization and assembly procedures, including review policy

10.4 Document inventory procedures, including review policy

11. Data Validation/Self Inspection Procedures

11.1 Data flow and chain-of-command for data review

11.2 Procedures for measuring precision and accuracy

11.3 Evaluation parameters for identifying systematic errors

11.4 Procedures to assure that hardcopy and diskette deliverables are complete and compliant with the requirements in Protocol Exhibits B and H.

11.5 Procedures to assure that hardcopy deliverables are in agreement with their comparable diskette deliverables.

11.6 Demonstration of internal QA inspection procedure (demonstrated by supervisory sign-off on personal notebooks, internal laboratory evaluation samples, etc.).

11.7 Frequency and type of internal audits (e.g., random, quarterly, spot checks, perceived trouble areas).

11.8 Demonstration of problem identification-corrective actions and resumption of analytical processing. Sequence resulting from internal audit (i.e., QA feedback).

11.9 Documentation of audit reports, (internal and external), response, corrective action, etc.

12. Data Management and Handling

12.1 Procedures for controlling and estimating data entry errors.

12.2 Procedures for reviewing changes to data and deliverables and ensuring traceability of updates.

12.3 Lifecycle management procedures for testing, modifying and implementing changes to existing computing systems including hardware, software, and documentation or installing new systems.

12.4 Database security, backup and archival procedures including recovery from system failures.

12.5 System maintenance procedures and response time.

12.6 Individuals(s) responsible for system operation, maintenance, data integrity and security.

12.7 Specifications for staff training procedures.

SOPS DELIVERY REQUIREMENTS:

Updating and submission of SOPs:

Within 60 days of contract award:

During the contract solicitation process, the Laboratory was required to submit their SOPs to BWAR. Within sixty (60) days after contract award, the Laboratory shall send a complete revised set of SOPs, fully compliant with the requirements of this Protocol, to the BWAR. The revised SOPs will become the official SOPs under the contract. The revised SOPs must include:

1) Changes resulting from A) the Laboratory's internal review of their procedures and B) the Laboratory's implementation of the requirements of the Protocol;

2) Changes resulting from the NYSDEC's review of the Laboratory evaluation sample data, bidder supplied documentation, and recommendations made during the pre-award On-Site laboratory evaluation.

Subsequent Submissions:

During the term of contract, the Laboratory shall amend the SOPs when the following circumstances occur:

1) The NYSDEC modifies the contract,

2) The NYSDEC notifies the Laboratory of deficiencies in their SOPs documentation

3) The NYSDEC notifies the Laboratory of deficiencies resulting from the NYSDEC's review of the Laboratory's performance,

4) The Laboratory's procedures change,

5) The Laboratory identifies deficiencies resulting from the internal review of their SOPs documentation, or

6) The Laboratory identifies deficiencies resulting form the internal review of their procedures.

The SOPs must be amended or new SOPs must be written within 30 days of when the circumstances listed above result in a discrepancy between what was previously described in the SOPs and what is presently occurring at the Laboratory's facility. All changes in the SOPs must be clearly marked (e.g., a bar in the margin indicating where the change is in the document, or highlighting the change by underlining the change, bold printing the change, or using a different print font). The amended/new SOPs must have the date on which the changes were implemented.

When the SOPs are amended or new SOPs are written, the Laboratory shall document in a letter the reasons for the changes, and submit the amended SOPs or new SOPs to the BWAR. The Laboratory shall send the letter and the amended sections of the SOPs or new SOPs within 14 days of the change. An alternate delivery schedule for the

submittal of the letter and amended/new SOPs may be proposed by the Laboratory, but it is the sole decision of the NYSDEC, represented by either the BWAR or the Project Officer, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Laboratory shall describe in a letter to the BWAR, why he/she is unable to meet the delivery schedule listed in this section. The BWAR will not grant an extension for greater than 30 days for amending/writing new SOPs. The BWAR will not grant an extension for greater than 14 days for submission of the letter documenting the reasons for the changes and for submitting amended/new SOPs. The Laboratory shall proceed and not assume that an extension will be granted until so notified by the BWAR.

The Laboratory shall send a complete set of current SOPs within 14 days of a request by the BWAR or to the recipients designated by the BWAR.

Corrective action:

If a Laboratory fails to adhere to the requirements listed in Exhibit E, Section III, a Laboratory may expect, but the NYSDEC is not limited to the following action: reduction of number of samples sent under this contract, suspension of sample shipment to the Laboratory, GC/MS tape audit, data package audit, On-Site laboratory evaluation, remedial laboratory evaluation sample, and/or contract sanction.

Section IV -- Data Management

Data management procedures are defined as procedures specifying the acquisition or entry, update, correction, deletion, storage and security of computer readable data and files. These procedures should be in written form and contain a clear definition for all databases and files used to generate or resubmit deliverables. Key areas of concern include: system organization (including personnel and security), documentation operations, traceability and quality control.

Data manually entered from hard-copy must be quality controlled and the error rates estimated. Systems should prevent entry of incorrect or out-of-range data and alert data entry personnel of errors. In addition, data entry error rates must be estimated and recorded on a monthly basis by reentering a statistical sample of the data entered and calculating discrepancy rates by data element.

The record of changes in the form of corrections and updates to data originally generated, submitted, and/or resubmitted must be documented to allow traceablilty of updates. Documentation must include the following for each change:

- Justification or rationale for the change.
- Initials of the person making the change or changes. Data changes must be implemented and reviewed by a person or group independent of the source generating the deliverable.
- Change documentation must be retained according to the schedule of the original deliverable.
- Resubmitted diskettes or other deliverables must be reinspected as a part of the laboratories' internal inspection process prior to resubmission. The entire deliverable, not just the changes, must be inspected.
- The Laboratory Manager must approve changes to originally submitted deliverables.
- Documentation of data changes may be requested by laboratory auditors.

Lifecycle management procedures must be applied to computer software systems developed by the laboratory to be used to generate and edit contract deliverables. Such systems must be thoroughly tested and documented prior to utilization.

- A software test and acceptance plan including test requirements, test results and acceptance criteria must be developed, followed, and available in written form.
- System changes must not be made directly to production systems generating deliverables. Changes must be made first to a development system and tested prior to implementation.
- Each version of the production system will be given an identification number, date of installation, date of last operation and archived.

- System and operations documentation must be developed and maintained for each system. Documentation must include a users manual and an operations and maintenance manual.

Individual(s) responsible for the following functions must be identified:

- System operation and maintenance including documentation and training.
- Database integrity, including data entry, data updating and quality control.
- Data and system security, backup and archiving.

Part III -- Requirements For Volatile Organics By GC/MS For Methods CLP, 624, And 8240

This Part outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with GC/MS determinations of low/medium concentration volatile organic TCL compounds in water and soil/sediment samples.. This section is not intended as a comprehensive quality control document, but rather as a guide to the specific QC operations that must be considered for volatile analyses. At a minimum, the Laboratory is expected to address these operations in preparing the Quality Assurance Program Plan and QA/QC Standard Operating Procedures discussed in Section II.

***NOTE**: When there is a conflict between the QA/QC requirements in a volatile organic analysis method in Exhibit D and those specified here in Exhibit E. Exhibit E requirements must be followed.*

These QC operations include the following:

- GC/MS Mass Calibration and Ion Abundance Pattern
- GC/MS Initial and Continuing Calibration
- Stability of Internal Standard Response and Retention Times
- Method Blank Analysis
- Holding Blank Analysis
- System Monitoring Compound Recoveries
- Matrix Spike and Matrix Spike Duplicate Analysis
- Matrix Spike Blank Analysis
- Dilution of Samples, Matrix Spikes, and Matrix Spike Duplicates

Not discussed in this section are the requirements for quality assurance of the data reporting aspects of volatile analyses which are described in general terms in Section II and III of this exhibit.

Section 1 -- GC/MS Mass Calibration and Ion Abundance Patterns

Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that a given GC/MS system meets the instrument performance criteria specified in Paragraph 1.1. The purpose of this instrument performance check is to assure correct mass calibration, mass resolution, and mass transmission. This is accomplished through the analysis of p-Bromofluorobenzene (BFB).

Definition: The twelve (12) hour time period for GC/MS mass calibration and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the BFB analysis that the Laboratory submits as documentation of a compliant instrument performance check. The time period ends after twelve (12) hours has elapsed according to the system clock.

1.1 p-Bromofluorobenzene (BFB)

1.1.1 Each GC/MS system used for the analysis of volatile TCL compounds must be mass calibrated to meet the ion abundance criteria listed in Table 1 for a maximum of a 50 nanogram injection of BFB. Alternately, add 50 ng of BFB solution to 5.0 mL of reagent water and analyze according to Exhibit D. BFB shall not be analyzed simultaneously with any calibration standards or blanks. This criterion must be demonstrated daily or for each twelve (12) hour time period, whichever is more frequent. If required, background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the Protocol specifications are unacceptable.

NOTE: All instrument conditions must be identical to those used in sample analysis, except that a different temperature program may be used.

1.1.2 BFB criteria MUST be met before any standards, samples, or blanks are analyzed. Any samples analyzed when mass calibration criteria have not been met may require reanalysis at no cost to the NYSDEC.

1.1.3 Whenever the Laboratory takes corrective action which may change or affect the mass calibration criteria for BFB (e.g., ion source cleaning or repair, etc.), the mass calibration must be verified irrespective of the 12-hour requirements.

TABLE 1. - BFB KEY IONS AND ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15.0 - 40.0 percent of the base peak
75	30.0 - 60.0 percent of the base peak
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of the base peak
173	less than 2.0 percent of mass 174
174	greater than 50.0 percent of the base peak
175	5.0 - 9.0 percent of mass 174
176	greater than 95.0 percent but less than 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

1.2 Documentation

Documentation of the calibration must be provided in the form of a bar graph plot and as a mass listing.

1.2.1 The Laboratory shall complete a Form V-VOA (Volatile Organic Instrument Performance Check) each time an analytical system is mass calibrated. In addition, all samples, standards, blanks, matrix spikes, matrix spike duplicates, and matrix spike blanks analyzed during a particular instrument performance check must be summarized on the bottom of the appropriate Form V. Detailed instructions for the completion of Form V are found in Exhibit B, Section III.

Section 2 -- GC/MS Initial Calibration for Target Compounds and System Monitoring Compounds

2. Summary

Prior to the analysis of samples and required blanks and after instrument performance criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations, analyzed consecutively under the same BFB tune, to determine the linearity of response utilizing standards for TCL compounds as specified in Exhibit C for the particular analytical method employed.

2.1 Prepare calibration standards as described in Exhibit D to yield the concentrations specified in the individual methods.

2.1.1 Initial calibration of volatile TCL compounds is required at five concentration levels as specified in the individual methods. System monitoring compounds shall be used with each of the calibration standards. If an analyte saturates at the 200 µg/L concentration level and the GC/MS system is calibrated to achieve a detection sensitivity of no less than 5 µg/L, the Laboratory must document it in the SDG Narrative and attach a quantitation report and RIC. In this instance, the Laboratory should calculate the results based on a four-point initial calibration for the specific analyte that saturates. The use of separate calibration methods which reflect the two different low and medium soil/sediment methods is required. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, document the reasons in the SDG Narrative. Analyze all blanks and standards under the same condition as the sample.

2.2 The NYSDEC has specified both the concentration levels for initial calibration and has also specified the specific internal standard to be used on a compound-by-compound basis for quantitation (see Tables 2 through 4). Establishment of standard calibration procedures is necessary and deviations by the Laboratory will not be allowed.

2.3 Analyze each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including all Protocol required system monitoring compounds. The relative retention times of each compound

in each calibration run should agree within 0.06 relative retention time. Late eluting compounds usually will have much better agreement.

Using Tables 1 through 3 and Equation 1, calculate the relative response factors (RRF) for each compound at each concentration level.

Equation 1

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standards from Table 1.

C_{is} = Concentration of the internal standard (µg/mL).

C_x = Concentration of the compound to be measured (µg/mL).

TABLE 2 - VOLATILE INTERNAL STANDARDS WITH CORRESPONDING CLP TARGET COMPOUNDS AND SYSTEM MONITORING COMPOUNDS ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloromethane	1,1,1-Trichloroethane	2-Hexanone
Bromomethane	Carbon tetrachloride	4-Methyl-2-pentanone
Vinyl chloride	Bromodichloromethane	Tetrachloroethene
Chloroethane	1,2-Dichloropropane	1,1,2,2-Tetrachloroethane
Methylene chloride	trans-1,3-Dichloropropene	Toluene
Acetone	Trichloroethene	Chlorobenzene
Carbon disulfide	Dibromochloromethane	Ethylbenzene
1,1-Dichloroethene	1,1,2-Trichloroethane	Styrene
1,1-Dichloroethane	Benzene	Xylenes (Total)
1,2-Dichloroethene (Total)	cis-1,3-Dichloropropene	Bromofluorobenzene (smc)
Chloroform	Bromoform	Toluene-d_8 (smc)
1,2-Dichloroethane		
2-Butanone		
1,2-Dichloroethane-d_4 (smc)		

(smc) = system monitoring compound

TABLE 3 - VOLATILE INTERNAL STANDARDS WITH CORRESPONDING METHOD 8240 TCL ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloromethane	1,1,1-Trichloroethane	2-Hexanone
Bromomethane	Carbon tetrachloride	4-Methyl-2-pentanone
Vinyl chloride	Vinyl acetate	Tetrachloroethene
Chloroethane	Bromodichloromethane	1,1,2,2-Tetrachloroethane
Methylene chloride	1,2-Dichloropropane	Toluene
Acetone	trans-1,3-Dichloropropene	Chlorobenzene
Carbon disulfide	Trichloroethene	Ethylbenzene
1,1-Dichloroethene	Dibromochloromethane	Styrene
1,1-Dichloroethane	1,1,2-Trichloroethane	Xylenes (Total)
trans-1,2-Dichloroethene	BenzeneBromofluorobenzene	
Chloroform	cis-1,3-Dichloropropene	(surr)
1,2-Dichloroethane	Bromoform	Toluene-d_8 (surr)
1,2-Dichloroethane-d_4 (surr)	2-Butanone	Ethyl methacrylate
Acrolein	2-Chloroethyl vinyl ether	1,2,3-Trichloropropane
Acrylonitrile	Dibromomethane	
Iodomethane	1,4-Dichloro-2-butene	
Trichlorofluoromethane		
Dichlorodifluoromethane		

(surr) = surrogate compound

TABLE 4 - VOLATILE INTERNAL STANDARDS WITH CORRESPONDING METHOD 624 TCL ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloromethane	1,1,1-Trichloroethane	Tetrachloroethene
Bromomethane	Carbon tetrachloride	1,1,2,2-Tetrachloroethane
Vinyl chloride	Bromodichloromethane	Toluene
Chloroethane	1,2-Dichloropropane	Chlorobenzene
Methylene chloride	trans-1,3-Dichloropropene	Ethylbenzene
1,1-Dichloroethene	Trichloroethene	1,3-Dichlorobenzene
1,1-Dichloroethane	Dibromochloromethane	1,2-Dichlorobenzene
trans-1,2-Dichloroethene	1,1,2-Trichloroethane	1,4-Dichlorobenzene
Chloroform	Benzene	Bromofluorobenzene (surr)
1,2-Dichloroethane	cis-1,3-Dichloropropene	Toluene-d_8 (surr)
1,2-Dichloroethane-d_4 (surr)	Bromoform	
Trichlorofluoromethane	2-Chloroethyl vinyl ether	

(surr) = surrogate compound

2.4 The calibration of the GC/MS is evaluated on the basis of the magnitude and stability of the relative response factors of each target compound and system monitoring compound.

2.4.1 Using the relative response factors (RRF) from the initial calibration, calculate the percent relative standard deviations (%RSD) for all calibration compounds using Equation 2 below.

Equation. 2

$$\%RSD = \frac{\text{Standard deviation}}{\text{mean}} \times 100$$

Where:

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}{n - 1}}$$

Where:

x_i = each individual value used to calculate the mean

$\overline{x}$ = the mean of n values

n = the total number of values

2.4.2 The response factors of the compounds listed below (Table 5) must meet the minimum RRF criteria at each concentration level and maximum %RSD criteria for the initial calibration, with allowance made for up to two volatile compounds. However, the RRFs for those two compounds must be greater than or equal to 0.010, and the %RSD of those two compounds must be less than or equal to 40.0% for the initial calibration to be acceptable.

2.4.3 Note that the following compounds have a Maximum %RSD of 100.%, and a Maximum %Difference of 100.%. These compounds must also meet a minimum RRF criteria of 0.010:

Acetone	1,2-Dichloropropane
2-Butanone	2-Hexanone
Carbon disulfide	Methylene chloride
Chloroethane	4-Methyl-2-pentanone
Chloromethane	Toluene-d_8
1,2-Dichloroethene (total)	1,2-Dichloroethane-d_4

2.4.4 A check of the calibration curve must be performed once every 12 hours (see Paragraph 1. for the definition of the twelve hour time period). Check the relative response factors of those compounds for which RRF values have been established. If these criteria are met, the relative response factors for all compounds are calculated and reported. A percent difference of the daily relative response factor (12 hour) compared to the average relative response factor from the initial curve is calculated. Calculate the percent difference for each compound and compare with the maximum percent difference criteria listed above. For negative percent difference values, the value must be greater than or equal to -25.0%, but less than 0%. As with the initial calibration, up to two volatile compounds in Table 2 may fail to meet the minimum RRF or maximum %D criteria, but the RRFs of those two compounds must be greater than or equal to 0.010, and the percent differences must be less than or equal to 40.0% for the continuing calibration to be acceptable.

2.4.5 Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 0.50 minutes (30 seconds) from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard

changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is required.

2.5 Each GC/MS system must be calibrated upon award of the contract, whenever the Laboratory takes corrective action which may change or affect the initial calibration criteria (i.e., ion source cleaning or repair, column removal or replacement, etc.), or if the continuing calibration acceptance criteria have not been met.

2.6 If time remains in the 12 hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard, if the initial calibration meets the calibration acceptance criteria above. A method blank is necessary. Quantify all sample results against the initial calibration standard that is the same concentration as the continuing calibration standard (50 µg/L).

2.7 If time does not remain in the 12-hour period beginning with the injection of the instrument performance check solution, a new injection of the instrument performance check solution must be made. If the new injection meets the ion abundance criteria for BFB, then a continuing calibration standard may be injected.

2.8 Documentation

Once the initial calibration is validated, calculate and report the average relative response factor ($\overline{RRF}$) and percent relative standard deviation (%RSD) for all TCL compounds or method analyte list. The Laboratory shall complete and submit a Form V-VOA (Volatile Organic Instrument Performance Check) and Form VI-VOA (Volatile Organic Initial Calibration) for each instrument used to analyze samples under this protocol. Detailed instructions for completion of Form VI-VOA are found in Exhibit B. The documentation also includes GC/MS data system printout for the analysis of each volatile calibration standard.

TABLE 5 - RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION OF VOLATILE ORGANIC COMPOUNDS

Volatile Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
Chloromethane	0.010	100.	100.
Bromomethane	0.100	20.5	25.0
Vinyl Chloride	0.100	20.5	25.0
Chloroethane	0.010	100.	100.
Methylene chloride	0.010	100.	100.
Acetone	0.010	100.	100.
Carbon disulfide	0.010	100.	100.
1,1-Dichloroethene	0.100	20.5	25.0
1,1-Dichloroethane	0.200	20.5	25.0
1,2-Dichloroethene (total)	0.010	100.	100.
Chloroform	0.200	20.5	25.0
1,2-Dichloroethane	0.100	20.5	25.0
1,2-Dichloroethane-d_4	0.010	100.	100.
2-Butanone	0.010	100.	100.
1,1,1-Trichloroethane	0.100	20.5	25.0
Carbon tetrachloride	0.100	20.5	25.0
Bromodichloromethane	0.200	20.5	25.0
1,2-Dichloropropane	0.010	100.	100.
cis-1,3-Dichloropropene	0.200	20.5	25.0
Trichloroethene	0.300	20.5	25.0
Dibromochloromethane	0.100	20.5	25.0
1,1,2-Trichloroethane	0.100	20.5	25.0
Benzene	0.500	20.5	25.0
trans-1,3-Dichloropropene	0.100	20.5	25.0
Bromoform	0.100	20.5	25.0
2-Hexanone	0.010	100.	100.
4-Methyl-2-pentanone	0.010	100.	100.
Tetrachloroethene	0.200	20.5	25.0
1,1,2,2-Tetrachloroethane	0.500	20.5	25.0
Toluene	0.400	20.5	25.0
Toluene-d_8	0.010	100.	100.
Chlorobenzene	0.500	20.5	25.0
Ethylbenzene	0.100	20.5	25.0
Styrene	0.300	20.5	25.0
Xylenes (total)	0.300	20.5	25.0
Bromofluorobenzene	0.200	20.5	25.0

Section 3. -- GC/MS Continuing Calibration for Target Compounds and System Monitoring Compounds.

Once the GC/MS system has been calibrated, the calibration must be verified each twelve (12) hour time period for each GC/MS system.

3.1 The concentration of the continuing calibration standard for volatile target compounds and system monitoring compounds is 50 µg/L.

3.2 A check of the calibration curve must be performed once every 12 hours (see Paragraph 1. for the definition of the twelve hour time period). Check the relative response factors of those compounds for which RRF values have been established. If these criteria are met, the relative response factors for all compounds are calculated and reported. A percent difference of the daily relative response factor (12 hour) compared to the average relative response factor from the initial curve is calculated. Calculate the percent difference for each compound and compare with the maximum percent difference criteria listed above. For negative percent difference values, the value must be greater than or equal to -25.0%, but less than 0%. As with the initial calibration, up to two volatile compounds in Table 2 may fail to meet the minimum RRF or maximum %D criteria, but the RRFs of those two compounds must be greater than or equal to 0.010, and the percent differences must be less than or equal to 40.0% for the continuing calibration to be acceptable.

3.3 The continuing calibration of the GC/MS system is evaluated on the basis of the magnitude of the relative response factors and the percent difference between the average RRF of each compound from the initial calibration and the RRF of that compound in the continuing calibration standard. The minimum RRF of each compound in the continuing calibration and the percent difference must meet the criteria given in Table 4. Allowance is made for any two volatile compounds that fail to meet these criteria. The minimum RRFs of those two compounds must be greater than or equal to 0.010, and the percent difference must be less than or equal to 40.0% for the continuing calibration to be acceptable.

3.4 The documentation includes Form VII VOA, a GC/MS data system printout for the analysis of the volatile calibration standard.

Section 4. -- Internal Standard Responses and Retention Times

The response of each of the internal standards in all calibration standards, samples, and blanks is crucial to the provision of reliable analytical results, because the quantitative determination of volatile compounds by these procedures is based on the use of internal standards added immediately prior to analysis.

4.1 The following compounds are used as internal standards, Chlorobenzene-d_5, and 1,4-Difluorobenzene in methanol at the concentration of 25.0 µg/mL for each internal standard. Addition of 10 µL of this spiking solution into 5.0 mL of sample or calibration standard results in a concentration of 50 µg/L.

4.2 The retention time and the extracted ion current profile (EICP) of each internal standard must be monitored for all analyses.

4.3 The area response of each internal standard from the EICP and the retention time of the internal standard must be evaluated for stability during or immediately after data acquisition. If the retention time for any internal standard changes by more than ±0.50 minutes (30 seconds) of its retention time from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. For samples analyzed during the same 12-hour period as the initial calibration standards, compare the internal standard responses and retention times against the 50 µg/L calibration standard. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

4.4 The documentation includes Form VIII VOA, and the GC/MS data system printout for the analysis of each sample, blank, matrix spike, matrix spike duplicate, matrix spike blank, and standard.

Section 5 -- Method Blank Analysis

A method blank is a volume of a clean reference matrix (deionized, distilled laboratory water for water samples, or a purified solid matrix for soil/sediment samples) that is carried through the entire analytical scheme. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of the blank is to determine the levels of contamination associated with the processing and analysis of samples.

5.1 For volatile analysis, a method blank must be analyzed once every twelve (12) hours, on each GC/MS system used for volatile analysis (see Paragraph 1. for the definition of the twelve hour time period).

5.1.1 For water samples, a volatile method blank consists of a 5 mL volume of reagent water spiked with the system monitoring compounds and internal standards, and carried through the analytical procedure.

5.1.1.1 An acceptable volatile method blank for water samples must contain less than or equal to five times (5x) the Contract Required Quantitation Limit (CRQL, see Exhibit C) of Methylene chloride, Acetone, and 2-Butanone, less than or equal to the CRQL of any other volatile target compound, and no TICs at greater than 10% of the nearest internal standard.

5.1.1.2 All volatile analyses associated with a blank that does not meet the requirements above, (i.e., a contaminated blank) must be repurged, reanalyzed, and reported at no additional cost to the NYSDEC.

5.1.1.3 The volatile method blank must be analyzed after the calibration standards, to ensure that there is no carryover of material from the standards into samples.

5.1.2 For medium level soil/sediment samples, a volatile method blank consists of 4 g of a purified solid matrix spiked with the system monitoring compounds, extracted with methanol, and carried through the analytical procedure.

5.1.2.1 An acceptable volatile method blank for medium level soil/sediment samples must contain less than or equal five times (5x) the Contract Required Quantitation Limit (CRQL, see Exhibit C) of Methylene chloride, Acetone, and 2-Butanone, less than or equal to the CRQL of any other volatile target compound, and no TICs greater than 10% of the nearest internal standard.

5.1.2.2 All volatile analyses associated with a blank that does not meet the requirements above, (i.e. a contaminated blank) must be repurged, reanalyzed, and reported at no additional cost to the NYSDEC.

5.1.2.3 The volatile method blank must be analyzed after the calibration standards, to ensure that there is no carryover of material from the standards into samples.

5.1.3 The Laboratory must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target compound at a level exceeding the initial calibration range, the Laboratory must either:

5.1.3.1 Analyze a method blank immediately after the contaminated sample. If an autosampler is used, a method blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The method blanks must meet the technical acceptance criteria for blank analysis, or

5.1.3.2 Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample and that exceeded the limits above. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If an autosampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample also must meet the maximum contamination criteria.

5.2 If a laboratory method blank exceeds these criteria, the Laboratory must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) MUST be re-extracted/re-purged and reanalyzed at no additional cost to the NYSDEC. The Laboratory Manager, or his designee, must address problems and solutions in the SDG Narrative (Exhibit B).

5.4 The documentation includes Form I VOA for the blank analysis, Form IV VOA, associating the samples and the blank, and a GC/MS data system printout for the analysis of the method blank.

Section 6 -- System Monitoring Compound Recoveries

The recoveries of the three system monitoring compounds are calculated from the analysis of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank. The purpose of the system monitoring compounds is to evaluate the performance of the entire purge and trap-gas chromatograph-mass spectrometer system. Poor purging efficiency, leaks, and cold spots in transfer lines are only a few of the potential causes of poor recovery of these compounds.

6.1 The system monitoring compounds are added to each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank prior to purging or extraction (medium soils only), at the following concentrations; Toluene-d_8, p-Bromofluorobenzene, and 1,2-Dichloroethane-d_4 are prepared in Methanol at a concentration of 25.0 µg/mL. Addition of 10.0 µL of this spiking solution into 5.0 mL of sample, results in a concentration of 50 µg/L.

6.2 Calculate the recovery of each system monitoring compound in all samples, blanks, matrix spikes, matrix spike duplicates and matrix spike blanks. Determine if recovery is within limits (see Table 6), and report on appropriate form.

6.2.1 Calculate the concentrations of the system monitoring compounds using the same equation as used for target compounds. Calculate the recovery of each system monitoring compound as follows:

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

6.2.2 If recovery of any one system monitoring compound is not within Protocol limits, the following are required:

- Check to be sure there are no errors in calculations, formulation of the system monitoring compound spiking solutions, and internal standards. Also, check instrument performance.
- Reanalyze the sample if none of the above steps reveal a problem.
- If an undiluted analysis with acceptable monitoring compound recoveries is being submitted, do not reanalyze diluted samples if the system monitoring compound recoveries are outside the limits.
- Never reanalyze the matrix spike, matrix spike duplicate, or matrix spike blank (MS/MSD/MSB), even if the system monitoring compound recoveries are outside the limits.
- If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications, it should be reanalyzed only if the MS/MSD system monitoring compound recoveries are within the limits. If the sample and associated MS/MSD show the same pattern

(i.e., outside the limits), then the sample does not require reanalysis and a reanalysis must not be submitted. Document in the narrative the similarity in recoveries of the system monitoring compounds in the sample and associated MS/MSD.

6.2.3 If the reanalysis of the sample solves the problem, then the problem was within the Laboratory's control. Therefore, only submit data from the analysis with system monitoring compound recoveries within the Protocol limits. This shall be considered the initial analysis, it shall be reported as such on all data deliverables, and it must meet holding time requirements specified in Exhibit I.

6.2.4 If the reanalysis of the sample does not solve the problem, (i.e., system monitoring compound recoveries are outside the Protocol limits for both analyses), then submit the data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes specified in Exhibit B.

6.2.5 If the sample with system monitoring compound recoveries outside the Protocol limits is the sample used for the matrix spike and matrix spike duplicate, and the system monitoring compound recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike, and matrix spike duplicate do not require reanalysis. Document in the narrative the similarity in system monitoring compound recoveries.

6.2.6 For medium level soil analyses, involving methanol extraction, the treatment of system monitoring compound recoveries is similar to that for semivolatile surrogate recoveries. If any system monitoring compound recovery is outside the limits, reanalyze the methanol extract first, to determine if the problem was with the analysis. If reanalysis of the extract does not solve the problem, then re-extract the medium soil sample and analyze the second extract.

6.2.7 Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, if the volatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

6.2.8 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the SDG Narrative.

6.2.9 If the recovery of any one system monitoring compound in a method blank is outside the limits, then the method and all associated samples must be reanalyzed at no additional cost to the NYSDEC.

6.3 The documentation includes Form II VOA, and a GC/MS data system printout for the analysis of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank.

TABLE 6
SYSTEM MONITORING COMPOUND RECOVERY LIMITS

%Recovery Compound	%Recovery Water	%Recovery Soil
Toluene-d_8	88 - 110	84 - 138
Bromofluorobenzene	86 - 115	59 - 113
1,2-Dichloroethane-d_4	76 - 114	70 - 121

Section 7 -- Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Analysis (MS/MSD/MSB)

In order to evaluate the effects of the sample matrix upon the methods used for volatile analyses, the NYSDEC has prescribed a mixture of volatile target compounds to be spiked into two aliquots of sample, and one aliquot of reagent water, and analyzed in accordance with the appropriate method.

7.1 A matrix spike and matrix spike duplicate must be performed on those samples so designated by the Contract Lab Sample Information Sheet. If no sample is so designated the Laboratory shall select a sample for spiking for each group of samples of a similar matrix, once:

- each SDG of field samples received, OR
- each 20 field samples in a SDG, OR
- each group of samples of a similar concentration level (soils only), OR
- each 7 calendar day period during which samples in an SDG were received (said period beginning with the receipt of the first sample in that SDG),

whichever is most frequent

UNLESS DIRECTED OTHERWISE BY BWAR OR THE PROJECT OFFICER.

A matrix spike blank must be prepared and analyzed each time MS/MSD samples are prepared to substantiate that any deviations in spike recovery are due to matrix effects and not improper spiking solutions.

7.2 Use the compounds listed in Table 7 to prepare matrix spiking solutions according to procedures described below. The analytical protocols for low/medium concentration volatile organics in Exhibit D require that a uniform amount of matrix spiking solution be added to the sample aliquots and to a matrix spike blank prior to

extraction/analysis. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate sample.

7.2.1 Volatile Matrix Standard Spiking Solution

7.2.1.1 Prepare a spiking solution in methanol that contains the following compounds at a concentration of 25.0 µg/mL: 1,1 Dichloroethene, Trichloroethene, Chlorobenzene, Toluene, and Benzene. Prepare fresh spiking solution weekly, or sooner, if the solution has degraded or evaporated.

7.2.1.2 Matrix spikes also serve as duplicates; therefore, add an aliquot of this solution to each of two portions from one sample chosen for spiking.

Table 7

Volatiles	
Chlorobenzene	1,1-Dichloroethene
Toluene	Trichloroethene
Benzene	

5.2.1 Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

5.3 Individual component recoveries for the matrix spike sample and blank are calculated using Equation 5.1.

Equation 5.1

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike Sample Results

SR = Sample Result

SA = Spike Added from spiking mix

5.4 Relative Percent Difference (RPD)

The Laboratory shall calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using Equation 5.2.

Equation 5.2

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

Where:

RPD = Relative Percent Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

5.5 Documentation

The matrix spike (MS) results (concentrations) for all volatile TCL compounds shall be reported on Form I-VOA (Volatile Organic Analysis Data Sheet) and the matrix spike percent recoveries shall be summarized on Form III-VOA (MS/MSD Recovery). These values will be used to periodically update existing performance based QC recovery limits (Table 8).

The results for all volatile TCL compounds in the matrix spike duplicate (MSD) analysis shall be reported on Form I-VOA (Volatile Organic Analysis Data Sheet) and the percent recovery and the relative percent difference shall be summarized on Form III-VOA (MS/MSD Recovery). See Exhibit B for detailed instructions on the completion of Form III-VOA.

The results for all volatile TCL compounds in the matrix spike blank analysis must meet the criteria in Table 9. If this criteria is not met, the MS/MSD/MSB must be re-prepared and reanalyzed. Results shall be reported on Form I-VOA (Volatile Organic Analysis Data Sheet) and the matrix spike percent recoveries shall be summarized on Form III-VOA (MS/MSD Recovery).

TABLE 8
MATRIX SPIKE RECOVERY AND
RELATIVE PERCENT DIFFERENCE LIMITS*

Compound	%Recovery Water	RPD Water	%Recovery Soil	RPD Soil
1,1-Dichloroethane	61-145	14	59-172	22

Trichloroethene	71-120	14	62-137	24
Benzene	76-127	11	66-142	21
Toluene	76-125	13	59-139	21
Chlorobenzene	75-130	13	60-133	21

TABLE 9
MATRIX SPIKE BLANK RECOVERY LIMITS*

Compound	%Recovery
1,1-Dichloroethane	61 - 145
Trichloroethene	71 - 120
Benzene	76 - 127
Toluene	76 - 125
Chlorobenzene	75 - 130

* These limits are for advisory purposes only. They are not to be used to determine if a sample should be reanalyzed. When sufficient multi-lab data are available, standard limits will be calculated.

7.2 The quality control limits for recovery and relative percent difference are given in Table 7. These limits are only advisory at this time, and no further action is required when the limits are exceeded.

7.3 The documentation includes Form I VOA for the MS, MSD and MSB analyses, Form III VOA, and a GC/MS printout for each analysis.

Section 8. -- Dilution of Samples, Matrix Spikes, and Matrix Spike Duplicates

If the on-column concentration of any sample exceeds the initial calibration range, that sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions are given below.

8.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.2 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

8.3 Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, if the volatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

8.4 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within calibration range. If the sample from which the MS/MSD aliquots were taken

contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the SDG Narrative.

8.5 For total Xylenes, where three isomers are quantified as two peaks, the calibration of each peak, should be considered separately, i.e., a diluted analysis is not required for total Xylenes unless the concentration of either peak separately exceeds 200 µg/L.

Part IV -- Requirements For Semivolatile Organics By GC/MS For Methods CLP, 625, And 8270

Parts II and III of this exhibit outline the requirements for the quality assurance program that each laboratory must establish under this Protocol. This Part outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with the determination of semi-volatile organic compounds in water and soil/sediment samples. This section is not intended as a comprehensive quality control document, but rather as a guide to the specific QC operations that must be considered for semivolatile analyses. At a minimum, the Laboratory is expected to address these operations in preparing the quality assurance plan and QA/QC Standard Operating Procedures discussed in Section II.

These QC operations are as follows:

- GC/MS Mass Calibration and Abundance Pattern
- GC/MS Initial and Continuing Calibration
- Stability of Internal Standard Response and Retention Times
- Method Blank Analysis
- Surrogate Recoveries
- Matrix Spike, Matrix Spike Duplicate, and Matrix Spike Blank Analysis
- Dilution of Samples, Matrix Spikes, and Matrix Spike Duplicates

Section 1 -- GC/MS Mass Calibration and Ion Abundance Patterns

1. Summary

Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that a given GC/MS system meets the instrument performance criteria specified below. The purpose of this instrument performance check is to assure correct mass calibration, mass resolution, and mass transmission. This is accomplished through the analysis of Decafluorotriphenylphosphine (DFTPP).

1.1 Each GC/MS system used for the analysis of semivolatile or pesticide compounds must be hardware tuned to meet the abundance criteria listed in Table 1. for a 50 ng injection of decafluorotriphenylphosphine (DFTPP). DFTPP may be analyzed separately or as part of the calibration standard. The criteria must be demonstrated daily or for each twelve (12) hour period, whichever is more frequent, before samples can be analyzed. DFTPP must be injected to meet this criteria. If required, background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the Protocol specifications are unacceptable.

***NOTE**: All instrument conditions must be identical to those used in sample analysis, except that a different temperature program may be used.*

1.2 The instrument performance check solution must be analyzed once at the beginning of each 12-hour period during which samples or standards are analyzed.

The twelve (12) hour time period for a GC/MS system instrument performance check and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after twelve (12) hours has elapsed according to the system clock.

1.3 The key ions produced during the analysis of DFTPP and their respective ion abundance criteria are given in Table 1.

TABLE 1
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA FOR QUADRAPOLE MASS SPECTROMETERS

Mass	Ion Abundance Criteria
51	30.0 - 60.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	40.0 - 60.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 1.00 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110.0 percent of mass 198
443	17.0 - 23.0 percent of mass 442

***NOTE**: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent that of m/z 198.*

Whenever the Laboratory takes corrective action which may change or affect the instrument performance criteria for DFTPP (e.g., ion source cleaning or repair, etc.), the mass calibration must be verified irrespective of the 12-hour calibration requirements.

1.4 Documentation

The Laboratory shall provide documentation of the calibration in the form of a bar graph spectrum and as a mass listing.

1.4.1 The Laboratory shall complete a Form V-CLP-SV (Semivolatile Organic Instrument Performance Check) each time an Instrument Performance Check is performed. In addition, all samples, standards, blanks, matrix spikes, and matrix spike duplicates analyzed during a particular 12-hour sequence must be summarized in chronological order on the bottom of the appropriate Form V-CLP-SV. Detailed instructions for the completion of Form V-SVA are found in Exhibit B, Section III.

Section 2 -- GC/MS Initial Calibration for Target Compounds and Surrogates

2. Summary

Prior to the analysis of samples and required blanks and after instrument performance criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations, analyzed consecutively under the same DFTPP Instrument Performance Check, to determine the linearity of response utilizing Superfund-TCL compound standards. A new initial calibration must be run whenever the continuing calibration does not meet criteria, or after major instrument maintenance is performed (e.g. cleaning ion source). The Laboratory must use the most recent initial calibration meeting criteria.

2.1 The levels of the initial calibration standards for semivolatile target compounds and surrogates are 20, 50, 80, 120, and 160 ng, in a 2 µL injection volume and are prepared as described in Paragraph 2.2.5 below.

2.2 The standards are to be analyzed according to the procedures given below.

2.2.1 Prior to the analysis of samples and required blanks, and after the instrument performance check solution criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations, analyzed in increasing concentration order, to determine instrument sensitivity and the linearity of GC/MS response for the semivolatile target compounds.

2.2.2 The internal standards are added to all calibration standards and all sample extracts (including blanks, matrix spikes, matrix spike duplicates, and matrix spike blanks) just prior to analysis by GC/MS. A 10 µL aliquot of the internal standard solution should be added to a 1 mL aliquot of calibration standards. The internal standards specified below should permit most of the semivolatile target compounds to have relative retention times of 0.80 to 1.20, using the assignments of internal standards to target compounds given in Table 2.

2.2.3 Internal standards - 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, Perylene-d_{12}.

An internal standard solution can be prepared by dissolving 100 mg of each compound in 50 mL of methylene chloride. It may be necessary to use 5 to 10 percent benzene or toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. The resulting solution will contain each standard at a concentration of 2000 µg/mL. A 10 µL portion of this solution should be added to each 1 mL of sample extract. This will result in 40 µg/mL of each internal standard in the 2 µL volume of extract injected into the GC/MS.

2.2.4 The quantitation ions for each internal standard are given in Table 3. Use the primary ion listed in Table 4 for quantitation, unless interferences are present. If interferences prevent the use of the primary ion for a given internal standard, use the secondary ion(s) listed in Table 4.

2.2.5 Prepare calibration standards at a minimum of five concentration levels (20, 50, 80, 120, 160 total ng per 2 µL). Each calibration standard should

contain each compound of interest and each surrogate. Eight compounds, 2,4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, and Pentachlorophenol will require only a four-point initial calibration at 50, 80, 120, and 160 total ng, since detection at less that 50 ng per injection is difficult. Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in screw-cap amber bottles with Teflon® liners. Fresh standards should be prepared every twelve months at a minimum. The continuing calibration standard should be prepared weekly and stored at 4°C (±2°C).

In order to facilitate the confirmation of pesticides and Aroclors from the semivolatile library search data, the Laboratory may wish to include the pesticide/Aroclor target compounds listed in Exhibit C in the semivolatile continuing calibration standard. The Laboratory may add any or all of these compounds to the semivolatile continuing calibration standard, but at a concentration of 10 µg/mL or less. If added to this GC/MS standard, these additional analytes are not reported on the semivolatile calibration form (Form VII), but must be included in the quantitation report for the continuing calibration standard. As only a single point calibration would be performed, no %RSD or percent difference criteria would apply to these additional analytes.

2.2.6 Analyze 2 µL of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. A 2 µL injection is required. Calculate relative response factors (RRF) for each compound using Equation 3.

Equation 3.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured (see Table 4).

A_{is} = Area of the characteristic ion for the specific internal standard (see Table 3).

C_{is} = Concentration of the internal standard (µg/mL).

C_x = Concentration of the compound to be measured (µg/mL).

TABLE 2 - SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING SUPERFUND-CLP TARGET COMPOUNDS AND SURROGATES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene
bis(2-Chloroethyl) ether	Isophorone	2 ,4, 6-Trichloro-phenol
2-Chlorophenol	2-Nltrophenol	2,4,5-Trichloro-phenol
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Chloronaphthalene
1,4-Dichlorobenzene	bis(2-Chloro-ethoxy)methane	2-Nitroaniline
1,2-Dichlorobenzene	2,4-Dichloro-phenol	Dimethyl phthalate
2-Methylphenol	1,2,4-Trichloro benzene	Acenaphthylene
2,2'-oxybis-(1-Chloropropane)	Naphthalene	3-Nitroaniline
4-Methylphenol	4-Chloroaniline	Acenaphthene
N-Nitroso-di-n-propylamine	Hexachloro-butadiene	2,4-Dinitrophenol
Hexachloroethane	4-Chloro-3-methylphenol	4-Nitrophenol
2-Fluorophenol (surr)	2-Methylnaphth-alene	Dibenzofuran
Phenol-d_5 (surr)	Nitrobenzene-d_5 (surr)	2,4-Dinitrotoluene
2-Chlorobenzene-d_4 (surr)		2,6-Dinitrotoluene
1, 2-Dichlorobenzene-d_4 (surr)		Diethyl phthalate
		4-Chlorophenyl phenyl ether
		Fluorene
		4-Nitroaniline
		2-Fluorobiphenyl (surr)
		2,4,6-Tribromo-phenol (surr)

surr = surrogate compound

TABLE 2 - SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING SUPERFUND-CLP TARGET COMPOUNDS AND SURROGATES ASSIGNED FOR QUANTITATION (continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4, 6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl-phthalate
N-Nitrosodi-phenylamlne	Butylbenzyl phthalate	Benzo(b)fluor-anthene
4-Bromophenyl phenyl ether	3,3'-Dichloro-benzidlne	Benzo(k)fluor-anthene
Hexachloro-benzene	Benzo(a)-anthracene	Benzo(a)pyrene
Pentachloro-phenol	bis(2-Ethyl-hexyl)phthalate	Indeno(1,2,3-cd)-pyrene
Phenanthrene	Chrysene	Dibenz(a,h)-anthracene
Carbazole	Terphenyl-d_{14} (surr)	Benzo(g,h,i)-perylene
Anthracene		
Di-n-butyl-phthalate		
Fluoranthene		

surr = surrogate compound

TABLE 3 - SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING METHOD 625 AND 8270 ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene
bis(2-Chloroethyl)ether	Isophorone	2,4,6-Trichlorophenol
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichlorophenol
1,3-Dichlorobenzene	2,4-Dimethylphenol	2-Chloronaphthalene
1,4-Dichlorobenzene	Benzoic acid	2-Nitroaniline
Benzyl alcohol	bis(2-Chloroethoxy)-methane	Dimethyl phthalate
1,2-Dichlorobenzene	2,4-Dichlorophenol	Acenaphthylene
2-Methylphenol	1,2,4-Trichlorobenzene	3-Nitroaniline
2,2'-oxybis(1-Chloro-propane)	Naphthalene	Acenaphthene
4-Methylphenol	4-Chloroaniline	2,4-Dinitrophenol
N-Nitroso-di-n-propylamine	Hexachlorobutadiene	4-Nitrophenol
Hexachloroethane	4-Chloro-3-methyl-phenol	Dibenzofuran
2-Fluorophenol (surr)	2-Methylnaphthalene	2,4-Dinitrotoluene
Phenol-d_6 (surr)	Nitrobenzene-d_5 (surr)	2,6-Dinitrotoluene
Aniline	Acetophenone	Diethyl phthalate
Ethyl methane sulfonate	2,6-Dichlorophenol	4-Chlorophenyl-phenyl ether
Methyl methane sulfonate	α,α-Dimethylphen-ethylamine	Fluorene
N-Nitrosodimethyl-amine	N-Nitrosodibutylamine	4-Nitroaniline
2-Picoline	N-Nitrosopiperidine	2-Fluorobiphenyl (surr)
		2,4,6-Tribromo-phenol (surr)
		1-Chloronaphthalene
		1-Naphthylamine
		2-Naphthylamine
		Pentachlorobenzene
		1,2,4,5-Tetrachloro-benzene
		2,3,4,6-Tetrachloro-phenol

TABLE 3 - SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING METHOD 625 AND 8270 ANALYTES ASSIGNED FOR QUANTITATION (continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4,6-Dinitro-2-methyl-phenol	Pyrene	Di-n-octylphthalate
N-Nitrosodiphenylamine	Butylbenzylphthalate	Benzo(b)fluoranthene
1,2-Diphenylhydrazine	3,3'-Dichlorobenzidine	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Benz(a)anthracene	Benzo(a)pyrene
Hexachlorobenzene	bis(2-Ethylhexyl) phthalate	Indeno(1,2,3-cd)-pyrene
Pentachlorophenol	Chyrsene	Dibenz(a,h)-anthracene
Phenanthrene	Benzo(g,h,i)perylene	Dibenz(a,j)acridine
Anthracene	Terphenyl-d_{14} (surr)	7,12-Dimethyl-benz(a)anthracene
Di-n-butylphthalate	Benzidine	3-Methylcholanthrene
Fluoranthene	p-Dimethylaminoazo-benzene	
4-Aminobiphenyl		
Diphenylamine		
Pentachloronitrobenzene		
Phenacetin		
Pronamide		

surr = surrogate compound

TABLE 4 - CHARACTERISTIC IONS FOR INTERNAL STANDARDS FOR SEMIVOLATILE COMPOUNDS

INTERNAL STANDARDS	Primary Ion	Secondary Ions
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenapthene-d_{10}	164	162,160
Phenanthrene-d_{10}	188	94,80
Chrysene-d_{12}	240	120,236
Perylene-d_{12}	264	260,265

TABLE 5 - CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS AND SURROGATES

Parameter	Primary Ion	Secondary Ion(s)
Phenol	94	65,66
bis(2-Chloroethyl)ether	93	63,95
2-Chlorophenol	128	64,130
1,3-Dichlorobenzene	146	148,113
1,4-Dichlorobenzene	146	148,113
1,2-Dichlorobenzene	146	148,113
2-Methylphenol	108	107
2,2'-oxybis(1-Chloropropane)	45	77,79
4-Methylphenol	108	107
N-Nitroso-di-propylamine	70	42,101,130
Hexachloroethane	117	201,199
Nitrobenzene	77	123,65
Isophorone	82	95,138
2-Nitrophenol	139	65,109
2,4-Dimethylphenol	107	121,122
bis(2-Chloroethoxy)methane	93	95,123
2,4-Dichlorophenol	162	164,98
1,2,4-Trichlorobenzene	180	182,145
Naphthalene	128	129,127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223,227
4-Chloro-3-methylphenol	107	144,142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235,272
2,4,6-Trichlorophenol	196	198,200
2,4,5-Trichlorophenol	196	198,200
2-Chloronaphthalene	162	164,127
2-Nitroaniline	65	92,138
Dimethyl phthalate	163	194,164
Acenaphthylene	152	151,153
3-Nitroaniline	138	108,92
Acenaphthene	153	152,154
2,4-Dinitrophenol	184	63,154
4-Nitrophenol	109	139,65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63,182
2,6-Dinitrotoluene	165	89,121

(continued)

TABLE 5 - CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS AND SURROGATES (continued)

Parameter	Primary Ion	Secondary Ion(s)
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Carbazole	167	166, 139
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzldine	252	254, 126
Benzo(a)anthracene	228	229, 226
bis(2-Ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-Octyl phthalate	149	---
Benzo(b)fluoranehene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
SURROGATES		
Phenol-d_5	99	42, 71
2-FluorophenoL	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-d_5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
2-Chlorophenol-d_4	132	68, 134
1,2-Dichlorobenzene-d_4	152	115, 150

2.3 The average relative response factor ($\overline{RRF}$) must be calculated for all compounds. Calculate the %Relative Standard Deviation (%RSD) of RRF values for the initial calibration using Equation 4:

Equation 4.

$$\%RSD = \frac{\text{Standard Deviation}}{\text{mean}} \times 100$$

Where:

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}{n - 1}}$$

Where:

x_i = each individual value used to calculate the mean

$\overline{x}$ = the mean of n values

n = the total number of values

2.4 Response factor criteria have been established for the calibration of the semivolatile target compounds and semivolatile surrogate compounds.

2.4.1 The response factors of the compounds listed in Table 6 must meet the minimum RRF criteria at each concentration level and maximum RSD criteria for the initial calibration, with allowance made for up to four semivolatile target and surrogate compounds. However, the RRFs for those four compounds must be greater than 0.010, and the %RSD of those four compounds must be less than or equal to 40.0% for the initial calibration to be acceptable.

TABLE 6 - RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION OF SEMIVOLATILE TARGET COMPOUNDS

Semivolatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Diff
Phenol	0.800	20.5	25.0
bis(2-Chloroethyl)ether	0.700	20.5	25.0
2-Chlorophenol	0.800	20.5	25.0
1,3-Dichlorobenzene	0.600	20.5	25.0
1,4-Dfchlorobenzene	0.500	20.5	25.0
1,2-Dichlorobenzene	0.400	20.5	25.0
2-Methylphenol	0.700	20.5	25.0
4-Methylphenol	0.600	20.5	25.0
N-Nitroso-di-propylamine	0.500	20.5	25.0
Hexachloroethane	0.300	20.5	25.0
Nitrobenzene	0.200	20.5	25.0
Isophorone	0.400	20.5	25.0
2-Nitrophenol	0.100	20.5	25.0
2,4-Dimethylphenol	0.200	20.5	25.0
bis(2-Chloroethoxy)methane	0.300	20.5	25.0
2,4-Dichlorophenol	0.200	20.5	25.0
1,2,4-Trichlorobenzene	0.200	20.5	25.0
Naphthalene	0.700	20.5	25.0
4-Chloro-3-methylphenol	0.200	20.5	2S.0
2-Methylnaphthalene	0.400	20.5	25.0
2,4,6-Trichlorophenol	0.200	20.5	25.0
2,4,5-Trlchlorophenol	0.200	20.5	25.0
2-Chloronaphthalene	0.800	20.5	25.0
Acenaphthylene	1.300	20.5	25.0
2,6-Dinitrotoluene	0.200	20.5	25.0
Acenaphthene	0.800	20.5	25.0
Dibenzofuran	0.800	20.5	25.0
2,4-Dinitrotoluene	0.200	20.5	25.0
4-Chlorophenyl-phenylether	0.400	20.5	25.0
Fluorene	0.900	20.5	25.0
4-Bromophenyl-phenylether	0.100	20.5	25.0
Hexachlorobenzene	0.100	20.5	25.0
Pentachlorophenol	0.050	20.5	25.0

(continued)

TABLE 6 - RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION OF SEMIVOLATILE TARGET COMPOUNDS (continued)

Semivolatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Diff
Phenanthrene	0.700	20.5	25.0
Anthracene	0.700	20.5	25.0
Fluoranehene	0.600	20.5	25.0
Pyrene	0.600	20.5	25.0
Benzo(a)anthracene	0.800	20.5	25.0
Chrysene	0.700	20.5	25.0
Benzo(b)fluoranthene	0.700	20.5	25.0
Benzo(k)fluoranthene	0.700	20.5	25.0
Benzo(a)pyrene	0.700	20.5	25.0
Indeno(1,2,3-cd)pyrene	0.500	20.5	25.0
Dibenzo(a,h)anthracene	0.400	20.5	25.0
Benzo(g,h,i)perylene	0.500	20.5	25.0
Nitrobenzene-d_5	0.200	20.5	25.0
2-Fluorobiphenyl	0.700	20.5	25.0
Terphenyl-d_{14}	0.500	20.5	25.0
Phenol-d_5	0.800	20.5	25.0
2-Fluorophenol	0.600	20.5	25.0
2-Chlorophenol-d_4	0.800	20.5	25.0
1,2-Dichlorobenzene-d_4	0.400	20.5	25.0

2.4.2 The following compounds have a Maximum %RSD of 100%, and a Maximum %Difference of 100%; and, these compounds must meet a minimum RRF criterion of 0.010:

2,2'-oxybis(1-Chloropropane)	4-Nitroaniline
4-Chloroaniline	4,6-Dinitro-2-methylphenol
Hexachlorobutadiene	N-Nitrosodiphenylamine
Hexachlorocyclopentatiene	Di-n-butylphthalate
2-Nitroaniline	Butylbenzylphthalate
Dimethylphthalate	3,3'-Dichlorobenzidine
3-Nitroaniline	bis(2-Ethylhexyl)phthalate
2,4-Dinitrophenol	Di-n-octylphthalate
4-Nitrophenol	2,4,6-Tribromophenol
Diethylphthalate	Carbazole

2.5 The calibration of the GC/MS is evaluated on the basis of the magnitude and stability of the relative response factors of each target compound and surrogate. The minimum RRF of each compound at each concentration level in the initial calibration and the percent relative standard deviation (%RSD) across all five points must meet the criteria given in Table 6. Allowance is made for any four semivolatile compounds that fail to meet these criteria. The minimum RRFs of those four

compounds must be greater than or equal to 0.010, and the %RSD must be less than or equal to 40.0% for the initial calibration to be acceptable.

2.6 The documentation includes Form VI-CLP-SV, a GC/MS data system printout for the analysis of each semivolatile calibration standard.

Section 3. -- GC/MS Continuing Calibration for Target Compounds and Surrogates.

Once the GC/MS system has been calibrated, the calibration must be verified each twelve (12) hour time period for each GC/MS system.

3.1 The level of the continuing calibration standard for semivolatile target compounds and surrogates is 50 ng, in a 2 µL injection volume, as described in Paragraph 2.2 above.

3.2 A check of the calibration curve must be performed once every 12 hours (see Paragraph 1.2 for the definition of the twelve-hour time period). Check the relative response-factors of those compounds for which RRF values have been established. If these criteria are met, the relative response factors for all compounds are calculated and reported. A percent difference of the daily relative response factor (12 hour) compared to the average relative response factor from the initial curve is calculated. Calculate the percent difference for each compound using Equation 5. and compare with the maximum percent difference criteria listed above.

Equation 5.

$$\% \text{ Difference} = \frac{\left| \overline{RRF_i} - RRF_c \right|}{\overline{RRF_i}} \times 100$$

Where:

$\overline{RRF_i}$ = average relative response factor from initial calibration.

RRF_c = relative response factor from current calibration check standard.

3.3 The continuing calibration of the GC/MS system is evaluated on the basis of the magnitude of the relative response factors and the percent difference between the average RRF of each compound from the initial calibration and the RRF of that compound in the continuing calibration standard. The minimum RRF of each compound in the continuing calibration and the percent difference must meet the criteria given in Table 6. Allowance is made for any four semivolatile compounds that fail to meet these criteria. The minimum RRFs of those four compounds must be greater than or equal to 0.010, and the %D must be less than or equal to 40.0% for the continuing calibration to be acceptable.

3.4 The documentation includes Form VII-CLP-SV, a GC/MS data system printout for the analysis of the semivolatile calibration standard.

Section 4. -- Internal Standard Responses and Retention Times

The response of each of the internal standards in all calibration standards, samples, and blanks is crucial to the provision of reliable analytical results because the quantitative determination of semivolatile compounds by these procedures is based on the use of internal standards added immediately prior to analysis.

4.1 The specific compounds used as internal standards are given in Paragraph 2.2.3. The amount of each internal standard in the injection volume (2 µL) of the sample extract analyzed by GC/MS must be 40 ng (20 µg/mL).

4.2 The retention time and the extracted ion current profile (EICP) of each internal standard must be monitored for all analyses.

4.3 TCL semivolatile organic components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte (see Tables 2 and 3). The EICP area of characteristic ions of analytes listed in Table 5 are used for quantitation. In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initializing and dating the changes made to the report.

Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 0.50 minutes (30 seconds) from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. For samples analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and retention times to those of the 50 ng calibration standard. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike blank, matrix spike, and matrix spike duplicate. The criteria are described in detail in the instructions for Form VIII, Internal Standard Area Summary. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. If the analysis of a subsequent sample or standard indicates that the system is functioning properly, then corrections may not be required. The samples or standards with EICP areas outside the limits must be re-analyzed, and treated according to 4.3.1 and 4.3.2 below. If corrections are made, then the Laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accomplished by the analysis of a standard or sample that does meet the EICP criteria. After corrections are made, the re-analysis of samples analyzed while the system was malfunctioning is required.

> **4.3.1** If after re-analysis, the EICP areas for all internal standards are inside the Protocol limits (-50% to +100%), then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, only submit data from the analysis with EICP's within the Protocol limits. This is considered the initial analysis, it must be reported as such on all data deliverables, and it must meet holding time requirements specified in Exhibit I.

4.3.2 If the re-analysis of the sample does not solve the problem, i.e., the EICP areas are outside the Protocol limits for both analyses, then submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables, using the sample suffixes specified in Exhibit B. Document in the SDG Narrative all inspection and corrective actions taken.

4.3.3 Do not re-analyze MS/MSD samples that do not meet the EICP area limits.

4.4 The documentation includes Form VIII SV, and the GC/MS data system printout for the analysis of each sample, blank, matrix spike, matrix spike duplicate, matrix spike blank and standard.

Section 5 -- Method Blank Analysis

A method blank is a volume of a clean reference matrix (deionized, distilled laboratory water for water samples, or a purified solid matrix (sodium sulfate) for soil/sediment samples), that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

5.1 Method blank analysis must be performed once for the following, on each GC/MS system used to analyze samples, whichever is most frequent:

- Each SDG, OR
- Each 7 calendar day period during which samples in an SDG are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), OR
- Each 20 samples in an SDG, including matrix spikes and reanalyses, that are of similar matrix (water or soil) or similar concentration (soil only), OR
- Whenever samples are extracted by the same procedure (continuous liquid-liquid extraction or sonication).

5.2 For the purposes of this Protocol, an acceptable method blank must meet the criteria in Paragraphs 5.2.1. and 5.2.2 below.

5.2.1 A method blank for semivolatile analysis must contain less than or equal to five times (5x) the Contract Required Quantitation Limit (CRQL, see Exhibit C) of the phthalate esters listed in Ex. C.

5.2.2 For all other target compounds, the method blank must contain less than or equal to the Contract Required Quantitation Limit (CRQL, see Exhibit C) of any single target compound.

5.3 If a method blank exceeds the limits for contamination above, the Laboratory must consider the analytical system out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) MUST be re-extracted and re-analyzed at no additional cost to the NYSDEC. The Laboratory Manager, or his designee, must address problems and solutions in the SDG Narrative (Exhibit B).

5.4 The documentation includes Form I-CLP-SV for the blank analysis, Form IV-CLP-SV, associating the samples and the blank, and a GC/MS data system printout for the analysis of the method blank.

Section 6 -- Surrogate Recoveries

The recoveries of the eight surrogates are calculated from the analysis of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank. The purpose of the surrogates is to evaluate the preparation and analysis of samples.

6.1 The surrogates are added to each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank prior to extraction. The compounds specified for this purpose are Phenol-d_5; 2,4,6-Tribromophenol; 2-Fluorophenol; Nitrobenzene-d_5; Terphenyl-d_{14}; 2-Fluorobiphenyl; 2-Chlorophenol-d_4; and 1,2-Dichlorobenzene-d_4. Additional surrogates may be added at the Laboratory's discretion.

6.2 Prepare a surrogate standard spiking solution that contains Nitrobenzene-d_5; Terphenyl-d_{14}; 2-Fluorobiphenyl; and 1,2-Dichlorobenzene-d_4 at a concentration of 100 µg/mL; Phenol-d_5; 2,4,6-Tribromophenol; 2-Fluorophenol; and Chlorophenol-d_4 at a concentration of 150 µg/mL. Store the spiking solutions at 4°C (±2°C) in Teflon®-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicate a problem.

6.3 Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits (see Table 7) and report on appropriate form.

6.3.1 Calculate the concentrations of the surrogate compounds using the same equations as used for the target compounds. Calculate the recovery of each surrogate as follows:

Equation 8.

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

6.3.2 Determine if the sample surrogate recovery meets specifications as follows:

- The eight semivolatile surrogates can be divided into three groups: base/neutral compounds (Nitrobenzene-d_5, 2-Fluorobiphenyl, and Terphenyl-d_{14}); acid compounds (Phenol-d_5, 2-Fluorophenol, and 2,4,6-Tribromophenol);

and compounds with advisory QC limits (2-Chlorophenol-d_4 and 1,2-Dichlorobenzene-d_4).

- If a single surrogate recovery from any group is not within the Protocol windows, the sample does not require reanalysis or re-extraction.

- If a single surrogate recovery from the base/neutral group and a single surrogate recovery from the acid group are not within the Protocol windows, the sample does not require reanalysis or re-extraction.

- Do not reanalyze or re-extract if only surrogates with advisory QC limits are not within the Protocol windows.

TABLE 7 - SURROGATE RECOVERY LIMITS

Compound	%Recovery Water	%Recovery Soil	
Nitrobenzene-d_5	35-114	23-120	
2-Fluorobiphenyl	43-116	30-115	
Terphenyl-d_{14}	33-141	18-137	
Phenol-d_5	10-110	24-113	
2-Fluorophenol	21-110	25-121	
2,4,6-Tribromophenol	10-123	19-122	
2-Chlorophenol-d_4	33-110	20-130	(advisory)
1,2-Dichlorobenzene-d_4	16-110	20-130	(advisory)

6.3.3 If the sample surrogate recovery does not meet specifications (i.e., if two base/neutral or two acid surrogates are out of limits or if recovery of any one base/neutral or acid surrogate is below 10%), the following are required:

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Reanalyze the sample if none of the above reveal a problem.
- If surrogate recoveries in a blank do not meet specifications, the blank may be reanalyzed alone.
- Do not reanalyze dilutions if surrogate recoveries are outside the limits.
- Never reanalyze the matrix spike or matrix spike duplicate (MS/MSD), even if surrogate recoveries are outside the limits.
- If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications, it should be reanalyzed only if the MS/MSD surrogate recoveries are within the limits. If the sample and associated MS/MSD show the same pattern (i.e., outside the limits), then the sample does not require re-analysis and a re-analysis must not be submitted.
- Document in the narrative the similarity in surrogate recoveries.

6.3.4 If the reanalysis of the sample solves the problem, then the problem was within the Laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the Protocol windows. This shall be considered the initial analysis, it shall be reported as such on all data deliverables, and it must meet holding time requirements specified in Exhibit I.

6.3.5 If none of the steps in 6.3.3 or 6.3.4 solve the problem, then reextract and reanalyze the sample. If the reextraction and reanalysis of the sample solves the problem, then the problem was within the Laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries

within the Protocol windows. This shall be considered the initial analysis, it shall be reported as such on all data deliverables, and it must meet holding time requirements specified in Exhibit I.

- If surrogate recoveries in a blank do not meet specifications even after reanalysis, all of the samples associated with that blank must be re-extracted along with the blank. The blank is intended to detect contamination in samples processed at the same time.

- Do not re-extract diluted samples if surrogate recoveries are outside the limits.

- Never re-extract the matrix spike or matrix spike duplicate (MS/MSD), even if surrogate recoveries are outside the limits.

- If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications after reanalysis, it should be re-extracted only if the reanalysis surrogate recoveries are not within the limits and MS/MSD surrogate recoveries are within the limits. If the sample and associated MS/MSD show the same pattern (i.e., outside the limits), then the sample does not require reanalysis and a reanalysis must not be submitted.

- Document in the narrative the similarity in surrogate recoveries.

6.3.6 If the re-extraction and reanalysis of the samples does not solve the problem, (i.e., the surrogate recoveries are outside the Protocol limits for both analyses), then submit the surrogate spike recovery data and the sample analysis data from analysis of both sample extracts. Distinguish between the initial analysis and the analysis of the re-extracted sample on all data deliverables, using the sample suffixes specified in Exhibit B.

6.4 The documentation includes Form II SV, and a GC/MS data system printout for the analysis of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank.

Section 7 -- Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Analysis (MS/MSD/MSB)

In order to evaluate the matrix effect of the sample upon the analytical methodology, the NYSDEC has prescribed a mixture of semivolatile target compounds to be spiked into two aliquots of a sample, and one aliquot of reagent water, and analyzed in accordance with the appropriate method.

7.1 A matrix spike, matrix spike duplicate, and matrix spike blank must be performed for each group of samples of a similar matrix, for the following, whichever is most frequent, unless directed differently by the Bureau of Program Services and Research or the Project Officer.

- Each SDG of field samples received, OR

- Each 20 field samples in a Case, OR

- Each group of field samples of a similar concentration level (soils only), OR

- Each 7 calendar day period during which field samples in a Case were received (said period beginning with the receipt of the first sample in that Sample Delivery Group).

Calculate the recovery of each matrix spike compound in the matrix spike, matrix spike duplicate, and matrix spike blank and report on appropriate form.

7.1.1 Calculate the concentrations of the matrix spike compounds using the same equations as used for target compounds. Calculate the recovery of each matrix spike compound using Equation 9.

Equation 9.

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike sample result

SR = Sample result

SA = Spike added

7.1.2 Calculate the relative percent difference of the recoveries of each compound in the matrix spike and matrix spike duplicate using Equation 10.

Equation 10.

$$RPD = \frac{|MSR - MSDR|}{(1/2)(MSR+MSDR)} \times 100$$

Where:

RPD = Relative Percent Difference

MSR = Matrix Spike Recovery

MSDR = Matrix Spike Duplicate Recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

7.1.3 The limits for matrix spike blank recovery are given in Table 8. These limits must be met. Failure to meet these limits will require re-extraction and reanalysis of the matrix spike, matrix spike duplicate and the matrix spike blank.

TABLE 8 - MATRIX SPIKE BLANK RECOVERY LIMITS

Compound	%Recovery
Phenol	12 - 110
2-Chlorophenol	27 - 123
1,4-Dichlorobenzene	36 - 97
N-Nitroso-di-n-propylamine	41 - 116
1,2,4-Trichlorobenzene	39 - 98
4-Chloro-3-methylphenol	23 - 97
Acenaphthene	46 - 118
4-Nitrophenol	10 - 80
2,4-Dinitrotoluene	24 - 96
Pentachlorophenol	9 - 103
Pyrene	26 - 127

7.1.4 The limits for matrix spike compound recovery and RPD are given in Table 9. As these limits are only advisory, no further action by the Laboratory is required, however, frequent failures to meet the limits for recovery or RPD warrant investigation by the Laboratory, and may result in questions from the NYSDEC.

TABLE 9 - MATRIX SPIKE RECOVERY AND
RELATIVE PERCENT DIFFERENCE LIMITS

Compound	%Recovery Water	RPD Water	%Recovery Soil	RPD Soil
Phenol	12-110	42	26- 90	35
2-Chlorophenol	27-123	40	25-102	50
1,4-Dichlorobenzene	36- 97	28	28-104	27
N-Nitroso-di-n-propylamine	41-116	38	41-126	38
1,2,4-Trichlorobenzene	39- 98	28	38-107	23
4-Chloro-3-methylphenol	23- 97	42	26-103	33
Acenaphthene	46-118	31	31-137	19
4-Nitrophenol	10- 80	50	11-114	50
2,4-Dinitrotoluene	24- 96	38	28- 89	47
Pentachlorophenol	9-103	50	17-109	47
Pyrene	26-127	31	35-142	36

7.2 The documentation includes Form I SV for the MS, MSD, and MSB analyses, Form III SV, and a GC/MS printout for each analysis.

Section 8. -- Dilution Of Samples, Matrix Spikes, and Matrix Spike Duplicates

If the on-column concentration of any compound in any sample exceeds the initial calibration range, that sample extract must be diluted, the internal standard concentration readjusted, and the sample extract reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

8.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.2 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

8.3 Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, if the semivolatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

8.4 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the SDG Narrative.

Part V -- Requirements For Pesticides And Aroclors By GC/ECD For Methods CLP, 608, And 8080

Parts II and III of this Exhibit outline the requirements for the quality assurance program that each laboratory must establish under this Protocol. This Part outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with all Exhibit D determinations of pesticide/Aroclor target compounds in water and soil/sediment samples. This section is not intended as a comprehensive quality control document, but rather as a guide to the specific QC operations that must be considered for pesticide/Aroclor analyses. At a minimum, the Laboratory is expected to address these operations in preparing the quality assurance plan and QA/QC Standard Operating Procedures discussed in Part II.

These QC operations include the following:

- GC Column Resolution
- GC/EC Initial and Continuing Calibration
- Determination of Retention Times and Retention Time Windows
- Analytical Sequence
- Blank analyses
- Matrix Spike, Matrix Spike Duplicate, and Matrix Spike Blank Analysis
- Dilution of Samples, Matrix Spikes, and Matrix Spike Duplicates

Not discussed in this section are the requirements for quality assurance of the data reporting aspects of pesticide/Aroclor analyses which are described in general terms in Section II and III of this exhibit.

Section 1. -- GC Column Resolution

Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that a given GC column meets the analyte resolution criteria. The purpose of this resolution check is to demonstrate that at the time of the initial calibration, the GC column is capable of chromatographically resolving the target compounds. This is accomplished through the analysis of the Resolution Check Mixture, which contains the nine target compounds that are most difficult to resolve.

1.1 The Resolution Check Mixture must be analyzed at the beginning of every initial calibration sequence, on each GC column and instrument used for analysis. Prepare the mixture of pesticides in hexane or iso-octane at the concentrations listed below. The mixture must be prepared every six months, or sooner if the solution has degraded or concentrated.

Resolution Check Mixture

gamma-Chlordane	10.0 ng/mL	Endrin ketone	20.0 ng/mL
Endosulfan I	10.0 ng/mL	Methoxychlor	100.0 ng/mL
p,p'-DDE	20.0 ng/mL	Tetrachloro-m-xylene	20.0 ng/mL
Dieldrin	20.0 ng/mL	Decachlorobiphenyl	20.0 ng/mL
Endosulfan sulfate	20.0 ng/mL		

1.2 The resolution criterion is that the depth of the valley between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0% of the height of the shorter peak. The poorest resolution on the DB-608 column probably will be between DDE and Dieldrin, between Methoxychlor and Endrin ketone and between Endosulfan I and gamma-Chlordane. On the DB-1701 column, resolution difficulties most frequently occur between Endosulfan I and gamma-Chlordane, and between Methoxychlor and Endosulfan sulfate.

1.3 Additional resolution criteria apply to the target compounds in the standards used for initial calibration and calibration verification.

1.3.1 All peaks in both of the Performance Evaluation Mixtures must be 100 percent resolved on both columns.

1.3.2 The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.

1.4 The documentation includes Form VI PEST-4, chromatograms and data system printouts for the analysis of the Resolution Check Mixture on each GC column and instrument used for analysis.

Section 2. -- GC/EC Initial Calibration For Target Compounds And Surrogates.

Prior to the analysis of samples and required blanks, the GC/EC system must be initially calibrated at a minimum of three concentrations to determine the linearity of response utilizing single component target compound and surrogate standards. Multicomponent target compounds are calibrated at a single point.

2.1 Individual Standard Mixtures A and B - the single component pesticide standards must be prepared in hexane or iso-octane at three concentrations for each analyte, including the surrogates. Two separate calibration mixtures, A and B, (listed below) are used to ensure that each peak is adequately resolved. The low point concentration corresponds to the CRQL for each analyte. The midpoint concentration must be 4 times the low point concentration. The high point concentration must be at least 16 times that of the low point, but a higher concentration may be chosen by the Laboratory. The high point concentration defines the upper end of the concentration range for which the concentration is valid. The solution must be prepared every six months, or sooner if the solution has degraded or concentrated.

Individual Standard Mixture A	Low Point Concentration
alpha-BHC	5.0 ng/mL
Heptachlor	5.0 ng/mL
gamma-BHC	5.0 ng/mL
Endosulfan I	5.0 ng/mL
Dieldrin	10.0 ng/mL
Endrin	10.0 ng/mL
p,p'-DDD	10.0 ng/mL
p,p'-DDT	10.0 ng/mL
Methoxychlor	50.0 ng/mL
Tetrachloro-m-xylene	5.0 ng/mL
Decachlorobiphenyl	10.0 ng/mL

Individual Standard Mixture B	Low Point Concentration
beta-BHC	5.0 ng/mL
delta-BHC	5.0 ng/mL
Aldrin	5.0 ng/mL
Heptachlor expoxide	5.0 ng/mL
alpha-Chlordane	5.0 ng/mL
gamma-Chlordane	5.0 ng/mL
p,p'-DDE	10.0 ng/mL
Endosulfan sulfate	10.0 ng/mL
Endrin aldehyde	10.0 ng/mL
Endrin ketone	10.0 ng/mL
Endosulfan II	10.0 ng/mL
Tetrachloro-m-xylene	5.0 ng/mL
Decachlorobiphenyl	10.0 ng/mL

2.2 Performance Evaluation Mixture (PEM) - prepare the PEM in hexane or iso-octane at the concentration levels listed below. The PEM must be prepared weekly, or more often if the solution has degraded or concentrated.

gamma-BHC	10.0 ng/mL	Endrin	50.0 ng/mL
alpha-BHC	10.0 ng/mL	Methoxychlor	250.0 ng/mL
4,4'-DDT	100.0 ng/mL	Tetrachloro-m-xylene	20.0 ng/mL
beta-BHC	10.0 ng/mL	Decachlorobiphenyl	20.0 ng/mL

2.3 The standards are to be analyzed using the following gas chromatographic analytical conditions. The conditions are recommended unless otherwise noted.

Carrier Gas:	Helium (Hydrogen may be used, see 2.3)
Column Flow:	5 mL/min
Make-up Gas:	P-5/P-10 or N2 (required)
Injector Temperature:	> 200°C (see 4.2)
Injection:	On-column
Injection Volume:	1 or 2 µL (see 4.1)
Injector:	Grob-type, splitless
Initial Temperature:	150°C
Initial Hold Time:	1/2 min
Temperature Ramp:	5°C to 6°C/min
Final Temperature:	275°C
Final Hold Time:	Until after Decachlorobiphenyl has eluted (approximately 10 minutes)

Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and MS/MSDs.

The linearity of the ECD may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

2.4 Initial Calibration Sequence

2.4.1 Before any samples are analyzed, it is necessary for the Laboratory to complete the initial calibration sequence given below.

2.4.2 Samples may be analyzed only after the initial calibration acceptance criteria (Paragraph 2.5) are met. Otherwise, the analytical system is not functioning adequately for use with this Protocol.

2.4.3 The initial calibration may continue to be used as long as the analytical system remains under control. The proof that the analytical system is under control is provided by the analyses of the Performance Evaluation Mixtures. If those analyses do not meet the criteria described in Paragraph 3., appropriate corrective action must be taken, and the initial calibration sequence must be repeated. The calibration sequence must also be repeated if any major change in instrument hardware or instrument parameters is made (e.g., if a new column is installed or if the detector temperature is changed).

***NOTE**: Steps 16 and 17 are used as part of the calibration verification as well (see Paragraph 3.).*

INITIAL CALIBRATION SEQUENCE

1. Resolution Check
2. Performance Evaluation Mixture
3. Aroclor 1016/1260
4. Aroclor 1221
5. Aroclor 1232
6. Aroclor 1242
7. Aroclor 1248
8. Aroclor 1254
9. Toxaphene
10. Low Point Standard A
11. Low Point Standard B
12. Midpoint Standard A
13. Midpoint Standard B
14. High Point Standard A
15. High Point Standard B
16. Instrument Blank
17. Performance Evaluation Mixture

2.5 Initial Calibration Acceptance Criteria (apply to each GC column independently)

2.5.1 The initial calibration sequence must be analyzed in the order listed in Paragraph 2.4 using the optimized GC/EC operating conditions described in Paragraph 2.3. The standards must be prepared according to Paragraph 2.1. Calculate the calibration factors and retention times as follows:

2.5.1.1 During the initial calibration sequence, the Laboratory must establish the magnitude of the linear ECD response range for each single component pesticide and surrogate on each column and for each GC system. This is accomplished by analyzing the Individual Standard Mixtures A and B at three concentrations during the initial calibration sequence in Paragraph 6.

2.5.1.2 The linearity of the instrument is determined by calculating a percent relative standard deviation (%RSD) of the calibration factors from a three-point calibration curve for each single component pesticide and surrogate. Either peak area or peak height may be used to calculate calibration factors used in the %RSD equation. For example, it is permitted to calculate linearity for Endrin based on peak area and to calculate linearity for Aldrin based on peak height. It is not permitted within a %RSD calculation for an analyte to use calibration factors calculated from both peak area and peak height. For example, it is <u>not</u> permitted to calculate the calibration factor for the low point standard for endrin using peak height and calculate the midpoint and high point standard calibration factors for endrin using peak area.

2.5.1.3 Calculate the calibration factor for each single component pesticide and surrogate over the initial calibration range using Equation 6. The calibration factors for the surrogates are calculated from the three analyses of Individual Standard Mixture A only.

2.5.1.4 Calculate the mean and the %RSD of the calibration factors for each single component pesticide and surrogate over the initial calibration range using Equations 1 and 2.

Equation 1.

$$CF = \frac{\text{Peak Area (or Height) of the Standard}}{\text{Mass Injected (ng)}}$$

Where:

CF = Calibration Factor

Equation 2.

$$\overline{CF} = \sum_{i=1}^{n} \frac{CF_i}{n}$$

2.5.2 The resolution criterion is that the depth of the valley between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0% of the height of the shorter peak. The poorest resolution on the DB-608 column probably will be between DDE and Dieldrin, between Methoxychlor and

Endrin ketone and between Endosulfan I and gamma-Chlordane. On the DB-1701 column, resolution difficulties most frequently occur between Endosulfan I and gamma-Chlordane, and between Methoxychlor and Endosulfan sulfate.

2.5.3 All peaks in both of the Performance Evaluation Mixtures must be 100 percent resolved on both columns.

2.5.4 The absolute retention times of each of the single component pesticides and surrogates in both of the PEMs must be within the retention time windows determined from the three-point initial calibration, in Paragraph 8.4.

2.5.5 The relative percent difference of the calculated amount and the true amount for each of the single component pesticides and surrogates in both of the PEMs must be less than or equivalent to 25.0 percent, using equation 5.

2.5.6 At least one chromatogram from each of the two Individual Standard Mixtures A and B, run during the initial calibration, must yield peaks that give recorder deflections of 50 to 100 percent of full scale.

2.5.7 The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.

2.5.8 The % RSD of the calibration factors for each single compound target compound must be less than or equal to 20.0 percent, except as noted below. The % RSD of the calibration factors for the two surrogates must be less than or equal to 30.0 percent. Up to two single component target compounds (but not surrogates) per column may exceed the 20.0 percent limit for %RSD, but those compounds must have a % RSD of less than or equal to 30.0 percent.

Equation 3.

$$\%\ RSD = \frac{\text{Standard Deviation}}{\overline{CF}} \times 100$$

Where:

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}{n-1}}$$

Where:

x_i = each individual value used to calculate the mean

$\overline{x}$ = the mean of n values

n = the total number of values

2.5.8.1 The linearity of the calibration is considered acceptable when the % RSD of the three point calibration is less than 20.0 percent except as noted in the following.

The % RSD of the two surrogates must be less than or equal to 30.0 percent. Up to two single compound target compounds (but not surrogates) per column may exceed the 20.0 percent limit for % RSD., but those compounds must have a % RSD of less than or equal to 30.0 percent.

2.5.8.2 If the linearity requirements listed above are met, the calibration factor from the mid point concentration standard is used for quantitation of each single component pesticide.

2.5.9 The breakdown of DDT and Endrin in both of the Performance Evaluation Mixtures must be less than 20.0 percent, and the combined breakdown of DDT and Endrin must be less than 30.0 percent where,

Equation 4.

$$\% \text{ Breakdown DDT} = \frac{\text{Amount found in ng (DDD+DDE)}}{\text{Amount in ng of DDT injected}} \times 100$$

Equation 5.

$$\% \text{ Breakdown Endrin} = \frac{\text{Amount found in ng (Endrin aldehyde + Endrin ketone)}}{\text{Amount of Endrin injected in ng}} \times 100$$

Equation 6.

Combined % Breakdown = %Breakdown DDT + %Breakdown Endrin

2.5.10 Toxaphene and Aroclors require only a single-point calibration and they present special analytical difficulties. Because of the alteration of these materials in the environment, it is probable that samples which contain multicomponent analytes will give patterns similar to, but not identical with, those of the standards.

2.5.11 A set of three to five major peaks is selected for each multicomponent analyte. Retention times and calibration factors are determined from the initial calibration analysis for each peak. Guidance for the choice of which peaks to use is given as follows:

2.5.11.1 The choice of the peaks used for multicomponent quantitation and the recognition of those peaks may be complicated by the

environmental alteration of the Toxaphene or Aroclors, and by the presence of coeluting analytes or matrix interferences, or both.

2.5.11.2 If more than one multicomponent analyte is observed in a sample, the Laboratory must choose separate peaks to quantitate the different multicomponent analytes. A peak common to both analytes present in the sample must not be used to quantitate either compound.

2.5.12 Sample analysis may not proceed until a satisfactory calibration has been demonstrated.

2.6 The documentation includes Form VI PEST, chromatograms and data system printouts of all standards for the pesticide/Aroclor calibration standards.

Section 3. -- GC/EC Continuing Calibration For Target Compounds And Surrogates.

Once the GC/EC system has been calibrated, the calibration must be verified each twelve (12) hour time period for each GC column and instrument used for analysis. The calibration is verified through the analysis of instrument blanks, Performance Evaluation Mixtures (PEM), and the mid point concentrations of Individual Standard Mixtures A and B.

3.1 Three types of analyses are used to verify the calibration and evaluate instrument performance. The analyses of instrument blanks, Performance Evaluation Mixtures (PEM), and the mid point concentration of Individual Standard Mixtures A and B constitute the continuing calibration. Sample data are not acceptable unless bracketed by acceptable analyses of instrument blanks, PEM, and both Individual Standard Mixtures A and B. The Performance Evaluation Mixtures and the Individual Standard Mixtures A and B are prepared as described in Paragraphs 2.1 and 2.2.

3.2 Instrument blank

3.2.1 An instrument blank is a hexane or iso-octane solution containing 20.0 ng/mL of tetrachloro-m-xylene and decachlorobiphenyl.

3.2.2 The first analysis in a 12-hour analysis sequence must be an instrument blank. All acceptable samples analyses are to be bracketed by acceptable instrument blanks, as described in Paragraph 3.3.

3.3 All acceptable samples must be analyzed within a valid analysis sequence as given below.

3.3.1 An acceptable instrument blank must be analyzed within a 12-hour analysis sequence and must demonstrate that no analyte in Exhibit C is detected at greater than 0.5 times the CRQL and that the surrogate retention times are within the retention time windows. For comparing the results of the instrument blank analysis to the CRQLs, assume that the material in the instrument resulted from the extraction of a 1 L water sample and calculate the concentration of each analyte using Equation 7. Compare the results to <u>one-half</u> the CRQL values for water samples in Exhibit C.

Equation 7.

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(Df)}{(CF)(V_o)(V_i)}$$

Where:

A_x = Area of the peak for the compound to be measured

CF = Calibration factor for the mid point concentration external standard (area per ng)

V_o = Volume of water extracted in milliliters (mL)

V_i = Volume of extract injected in microliters (µL). (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto to each column.)

V_t = Volume of the concentrated extract in microliters (µL) (this volume must be 10,000 µL)

Df = Dilution Factor. The dilution factor for analysis of water samples by this method is defined as follows:

$$Df = \frac{\mu L \text{ most conc. extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most conc. extract used to make dilution}}$$

If no dilution is performed, Df = 1.0.

3.3.2 If analytes are detected at greater than half the CRQL, or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. After an acceptable instrument blank is run, all samples which were run after the last acceptable instrument blank must be reinjected during a valid run sequence at no additional cost to the NYSDEC and must be reported.

3.3.3 Analysts are cautioned that running an instrument blank once every 12 hours is the minimum Protocol requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks more often to avoid discarding data.

Time	Injection #	Material Injected

	1 - 15	First 15 steps of the initial calibration
0 hr.	16	Instrument blank at end of initial calibration
	17	PEM at end of initial calibration
	18	First sample
	0	Subsequent samples
	0	
	0	
12 hr.	0	Last sample
	1st injection past	Instrument blank
	12:00 hr.	
	2nd and 3rd	Individual Standard Mixtures
	injections past	A and B
	12:00 hr.	
	0	Sample
	0	
	0	
	0	Subsequent samples
	0	
Another 12 hr.	0	Last sample
	1st injection past	Instrument blank
	12 hr.	
	2nd injection	PEM
	0	Sample
	0	
	0	Subsequent samples
	0	

Time	Injection #	Material Injected
Another 12 hr.	0	Last sample
	1st injection past	Instrument blank
	12:00 hr.	
	2nd and 3rd	Individual Standard Mixtures
	injections past	A and B
	12:00 hr.	
	0	Sample
	0	
	0	
	0	Subsequent samples
	0	
	etc.	

***NOTE**: The first 12 hours are counted from the injection #16 (the Instrument Blank at the end of the initial calibration sequence), not from injection #1. Samples may be injected until 12:00 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. Because the 12-hour time period is timed from injection of the instrument blank until the injection of the last sample, each 12-hour period may be separated by the length of one chromatographic run, that of the analysis of the last sample. While the 12-hour period may not be exceeded, the Laboratory may run instrument blanks and standards more frequently, for instance to accommodate staff working on 8-hour shifts.*

3.4 An instrument blank and the Performance Evaluation Mixture must bracket one end of a 12-hour period during which sample data are collected, and a second instrument blank and the mid point concentration of Individual Standard Mixtures A and B must bracket the other end of the 12-hour period.

3.5 For the 12-hour period immediately following the initial calibration sequence, the instrument blank and the PEM that are the last two steps in the initial calibration sequence bracket the front end of that 12-hour period. The injection of the instrument blank starts the beginning of that 12-hour period. Samples may be injected for 12 hours from the injection of the instrument blank. The three injections immediately after that 12-hour period must be an instrument blank, Individual Standard Mixture A, and Individual Standard Mixture B. The instrument blank must be analyzed first, before either standard. The Individual Standard Mixtures may be analyzed in either order (A,B or B,A).

3.6 The analyses of the instrument blank and Individual Standard Mixtures A and B immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided that they meet the acceptance criteria. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a PEM, in that order. Those two analyses may in turn be used to

bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks, PEMs, or Individual Standard Mixtures fails to meet the acceptance criteria. The 12-hour time period begins with the injection of the instrument blank. Standards (PEM or Individual Standard Mixtures), samples and required blanks may be injected for 12:00 hours from the time of injection of the instrument blank.

3.7 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an acceptable instrument blank and PEM must be analyzed in order to start a new sequence. This requirement applies even if no analyses were performed since that standard(s) was injected.

3.8 After a break in sample analyses, the Laboratory may only resume the analysis of samples using the current initial calibration for quantitation by analyzing an acceptable instrument blank and a PEM.

3.9 If the entire 12-hour period is not required for the analyses of all samples to be reported and all data collection is to be stopped, the incomplete sequence must be ended with either the instrument blank/PEM combination or the instrument blank/Individual Standard Mixtures A and B combination, whichever was due to be performed at the end of 12-hour period.

3.10 Analysts are cautioned that running an instrument blank and a performance evaluation mixture once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable, and will result in the rejection of data. Therefore, it may be necessary to run instrument blanks and performance evaluation mixtures more often to avoid discarding data.

3.11 The requirements for running the instrument blanks, Performance Evaluation Mixture, and Individual Standard Mixtures A and B are waived when no samples, method blanks, or matrix spikes are run during that 12-hour period. After a break in sample analysis, the Laboratory may resume the analysis of samples, method blanks, and matrix spikes and may use the current initial calibration for quantitation only after an acceptable PEM is run. If a successful PEM cannot be run after an interruption, an acceptable initial calibration must be run before sample data may be collected. All acceptable sample analyses must be bracketed by acceptable performance evaluation mixtures and instrument blanks.

3.12 Technical Acceptance Criteria (apply to each GC column independently)

3.12.1 All single component pesticides and surrogates in the Performance Evaluation Mixtures used to demonstrate continuing calibration must be 100 percent resolved. The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.

3.12.2 The absolute retention time for each of the single component pesticides and surrogates in the PEMs and mid point concentration of the Individual Standard Mixtures used to demonstrate continuing calibration must be within the retention time window determined from the three-point initial calibration.

3.12.3 The relative percent difference of the calculated amount and the true amount for each of the single component pesticides and surrogates in the PEM and mid point concentration of the Individual Standard Mixtures used to demonstrate continuing calibration must be less than or equal to 25.0 percent, using Equation 8.

Equation 8.

$$RPD = \frac{|C_{nom} - C_{calc}|}{C_{nom}} \times 100$$

C_{nom} = true concentration of each analyte

C_{calc} = calculated concentration of each analyte from the analyses of the standard

***Note**: The vertical bars in the equation indicate the absolute value, hence RPD is always a positive number.*

3.12.4 The percent breakdown of DDT and Endrin in the PEM must be less than or equal to 20.0 percent on both columns. The combined breakdown of DDT and Endrin must be less than or equal to 30.0 percent on both columns.

3.12.5 All instrument blanks must meet the acceptance criteria in Paragraph 7.4.

3.13 The continuing calibration is evaluated on the basis of the stability of the retention times of the target compounds in the standards.

3.14 The continuing calibration is evaluated on the basis of the stability of the instrument response to the target compounds in the PEM, as judged by the reproducibility of the determinations of the concentrations of these compounds in the standard.

3.15 The continuing calibration is evaluated on the basis of the extent of breakdown of two target compounds in the PEM, Endrin and 4,4'-DDT, as described in Paragraph 2.4.9.

3.16 The continuing calibration is evaluated on the basis of the levels of contamination that are found in the instrument blank.

3.16.1 An acceptable instrument blank must be analyzed within a 12-hour analysis sequence and must demonstrate that no analyte in Exhibit C is detected at greater than 0.5 times the CRQL and that the surrogate retention times are within the retention time windows. For comparing the results of the instrument blank analysis to the CRQLs, assume that the material in the instrument resulted from the extraction of a 1 L water sample and calculate the

concentration of each analyte using Equation 9. Compare the results to one-half the CRQL values for water samples in Exhibit C.

Equation 9.

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(Df)}{(CF)(V_o)(V_i)}$$

Where:

A_x = Area of the peak for the compound to be measured

CF = Calibration factor for the mid point concentration external standard (area per ng)

V_o = Volume of water extracted in milliliters (mL)

V_i = Volume of extract injected in microliters (µL). (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto to each column.)

V_t = Volume of the concentrated extract in microliters (µL) (this volume must be 10,000 µL).

Df = Dilution Factor. The dilution factor for analysis of water samples by this method is defined as follows:

$$Df = \frac{\mu L \text{ most conc. extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most conc. extract used to make dilution}}$$

If no dilution is performed, Df = 1.0.

3.16.2 If analytes are detected at greater than half the CRQL, or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. After an acceptable instrument blank is run, all samples which were run after the last acceptable instrument blank must be reinjected during a valid run sequence at no additional cost to the NYSDEC and must be reported.

3.17 The documentation includes Form VII PEST, Form VIII PEST, chromatograms and data system printouts for all standards and instrument blanks analyzed.

Section 4. -- Determination Of Retention Times and Retention Time Windows

The identification of single component pesticides by gas chromatographic methods is based primarily on retention time data. The identification of multicomponent analytes is

based primarily on recognition of patterns of retention times displayed on a chromatogram. Therefore, the determination of retention times and retention time windows is crucial to the provision of valid data for these target compounds.

4.1 The identification of all Pesticide/Aroclor target compounds analyzed by the procedures described in Exhibit D, is based on the use of absolute retention time. The mean retention time of each target compound, or each peak in a multicomponent target compound, is determined from the initial calibration standards, according to Equation 10.

Equation 10.

$$\overline{RT} = \sum_{i=1}^{3} \frac{RT_i}{3}$$

Section 5. -- Determination of Absolute Retention Times.

5.1 During the initial calibration sequence, absolute retention times (RT) are determined for all single response pesticides, the surrogates, and at least three major peaks of each multicomponent analyte.

5.2 For single component pesticides, an RT is measured in each of three calibration standards and the mean RT is calculated as the average of the three values. An RT is measured for the surrogates in each of the three analyses of Individual Mixture A during the initial calibration and the mean RT is calculated as the average of the three values using Equation 10. above.

5.3 A retention time window is calculated for each single component analyte and surrogate by using the list in Paragraph 5.8. Windows are centered around the mean absolute retention time for the analyte established during the initial calibrations.

5.4 For each multicomponent analyte, the RTs for three to five peaks are calculated from the initial calibration standard analysis. An RT window of ±0.07 minutes is used for all multicomponent analyte peaks.

5.5 Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.

5.6 The retention time shifts of the surrogates are used to evaluate the stability of the gas chromatographic system during analysis of samples and standards. The retention time of the surrogates must be within the retention time windows determined in Paragraphs 5.3.

5.7 The documentation includes Form VI PEST, Form VII PEST, Form VIII PEST, chromatograms and data system printouts for all standards for the Pesticide/Aroclor initial and continuing calibrations, on each instrument and GC column used for analysis.

5.8 Retention time windows for single and multicomponent analytes and surrogates.

Compound	Retention Time Window (in Minutes)
alpha-BHC	±0.05
beta-BHC	±0.05
gamma-BHC	±0.05
delta-BHC	±0.05
Heptachlor	±0.05
Aldrin	±0.05
alpha-Chlordane	±0.07
gamma-Chlordane	±0.07
Heptachlor epoxide	±0.07
Dieldrin	±0.07
Endrin	±0.07
Endrin aldehyde	±0.07
Endrin ketone	±0.07
DDD	±0.07
DDE	±0.07
DDT	±0.07
Endosulfan I	±0.07
Endosulfan II	±0.07
Endosulfan sulfate	±0.07
Methoxychlor	±0.07
Aroclors	±0.07
Toxaphene	±0.07
Tetrachloro-m-xylene	±0.05
Decachlorobiphenyl	±0.10

Section 6. -- Analytical Sequence

6.1 The standards and samples analyzed according to the procedures in Exhibit D must be analyzed in a sequence described in Paragraph 3.3. This sequence includes requirements that apply to the initial and continuing calibrations, as well as to the analysis of samples. The documentation includes Form VIII PEST.

6.2 Before any samples are analyzed, it is necessary for the Laboratory to complete an acceptable initial calibration sequence (see Paragraph 2).

6.3 After the initial calibration, the analysis sequence may continue as long as acceptable instrument blanks, Performance Evaluation Mixtures, and Individual Standard Mixtures A and B are analyzed at the required frequency (see Paragraph 2.4.3). This analysis sequence shows only the minimum required blanks and standards. More blanks and standards may be run at the discretion of the Laboratory; these must also satisfy the criteria presented in Paragraph 7 in order to continue the run sequence.

6.4 An analysis sequence must also include all required matrix spike/matrix spike duplicate/matrix spike blank analyses and method blanks, but the Laboratory may decide at what point in the sequence they are to be analyzed.

6.5 A standard of any identified Aroclor must be run within 72 hours of its detection in a sample chromatogram.

Section 7. -- Blank Analysis

There are three types of blanks always required by this method: the method blank, the matrix spike blank, and the instrument blank. A separate sulfur cleanup blank may be required if all samples associated with a given method blank are not subjected to sulfur cleanup. Samples that are associated with a sulfur cleanup blank are also associated with the method blank with which they were extracted. Both the method and sulfur cleanup blanks must meet the respective acceptance criteria for the sample analysis acceptance criteria to be met.

7.1 Method blank

7.1.1 Method blanks are spiked with the surrogate solution, extracted, cleaned up, and analyzed by following the same procedure that is used with the samples. A water method blank is one liter of reagent water treated as the water sample aliquot. A soil method blank is 30 g of sodium sulfate treated as the soil sample aliquot.

Method blank analysis must be performed once for the following, whichever is most frequent, and analyzed on each GC/EC system used to analyze samples:

- Each SDG, OR
- Each 7 calendar day period during which samples in an SDG are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), OR
- Each 20 samples in an SDG, including matrix spikes and reanalyses, that are of similar matrix (water or soil), OR
- Whenever samples are extracted by the same procedure (separatory funnel, Soxhlet, continuous liquid-liquid extraction, or sonication).

7.1.2 In order to be acceptable, a method blank analysis cannot contain any of the analytes listed in Exhibit C at greater than the CRQL. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl.

7.1.3 All samples associated with an unacceptable method blank (see Form IV) must be reextracted and reanalyzed at no additional cost to the NYSDEC.

7.2 Matrix Spike Blank

7.2.1 Matrix spike blanks are spiked with the surrogate solution and the matrix spiking solution, extracted, cleaned up, and analyzed by following the same procedure that is used with the samples. A water matrix spike blank is one liter of reagent water treated as the water sample aliquot. A soil matrix spike blank is 30 g of sodium sulfate treated as the soil sample aliquot.

Matrix spike blank analysis must be performed once for each matrix spike/matrix spike duplicate analysis (see Paragraph 9.)

7.2.2 In order to be acceptable, a matrix spike blank analysis must meet the recovery limits below. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl.

MATRIX SPIKE BLANK RECOVERY LIMITS

Compound	%Recovery Water	%Recovery Soil
gamma-BHC (Lindane)	56-123	46-127
Heptachlor	40-131	35-130
Aldrin	40-120	34-132
Dieldrin	52-126	31-134
Endrin	56-121	42-139
4,4'-DDT	38-127	23-134

7.2.3 All samples associated with an unacceptable matrix spike blank (see Form IV) must be reextracted and reanalyzed at no additional cost to the NYSDEC.

7.3 Sulfur Cleanup Blank.

7.3.1 The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup procedure.

7.3.2 The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur cleanup blank is associated with the part of the set which required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then the method blank must be subjected to sulfur cleanup, and no separate sulfur cleanup blank is required.

7.3.3 In order to be acceptable, a sulfur blank analysis cannot contain any of the analytes listed in Exhibit C at greater than the CRQL, assuming that the material in the sulfur blank resulted from the extraction of a 1 L water sample. Calculate the concentration of each analyte using the equation in Paragraph 3.3.1. Compare the results to the CRQL values for water samples in Exhibit C. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl.

7.3.4 All samples associated with an unacceptable sulfur blank (see Form IV) must be reextracted and reanalyzed at no additional cost to the NYSDEC.

7.4 Instrument blank

7.4.1 An instrument blank is a hexane or iso-octane solution containing 20.0 ng/mL of tetrachloro-m-xylene and decachlorobiphenyl.

7.4.2 The first analysis in a 12-hour analysis sequence must be an instrument blank. All acceptable samples analyses are to be bracketed by acceptable instrument blanks, as described in Paragraph 3.2.

7.4.3 An acceptable instrument blank must be analyzed within a 12-hour analysis sequence and must demonstrate that no analyte in Exhibit C is detected at greater than 0.5 times the CRQL and that the surrogate retention times are within the retention time windows. For comparing the results of the instrument blank analysis to the CRQLs, assume that the material in the instrument resulted from the extraction of a 1 L water sample and calculate the concentration of each analyte using the equation in Paragraph 3.3.1. Compare the results to <u>one-half</u> the CRQL values for water samples in Exhibit C.

7.4.4 If analytes are detected at greater than half the CRQL, or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. After an acceptable instrument blank is run, all samples which were run after the last acceptable instrument blank must be reinjected during a valid run sequence at no additional cost to the NYSDEC and must be reported.

7.4.5 Analysts are cautioned that running an instrument blank once every 12 hours is the minimum Protocol requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or

if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks more often to avoid discarding data.

Section 8. -- Surrogate Recoveries

The recoveries of the two surrogates are calculated from the analysis on each GC column of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank. The purpose of the surrogates is to evaluate the preparation and analysis of samples.

8.1 The surrogates are added to each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank prior to extraction, at the concentrations described below.

8.1.1 Surrogate solution - the surrogates, Tetrachloro-m-xylene and Decachlorobiphenyl, are added to all standards, samples, matrix spikes, and blanks. Prepare a surrogate spiking solution of 0.2 µg/mL of each of the two compounds in acetone. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner, if comparison with quality control check samples indicates a problem.

***CAUTION**: Analysts must allow all spiking solutions to equilibrate to room temperature before use.*

8.2 The concentrations of the surrogates are calculated separately for both GC columns in a similar manner as the other analytes, using Equations 13 and 14. Use the calibration factors from the midpoint concentration of Individual Standard Mixture A. The recoveries of the surrogates are calculated for both GC columns according to Equation 11.

Equation 11.

$$\text{Surrogate Percent Recovery} = \frac{Q_d}{Q_a} \times 100$$

Where,

Q_d = Quantity determined by analysis

Q_a = Quantity added to sample/blank

The limits for the recovery of the surrogates are 30-150 percent for both surrogate compounds. As these limits are only advisory, no further action is required by the Laboratory is required, however, frequent failures to meet the limits for surrogate recovery warrant investigation by the Laboratory, and may result in questions from the NYSDEC. Surrogate recovery data from both GC columns are reported (see Exhibit B).

8.3 The quality control limits for surrogate recovery are 30-150 percent. These limits are only advisory, and no further action by the Laboratory is required if the limits

are exceeded, however, frequent failures to meet the limits for surrogate recovery warrant investigation by the Laboratory, and may result in questions from the NYSDEC.

8.4 The documentation includes Form II PEST, a chromatogram and a GC/EC data system printout for the analysis of each sample, blank, matrix spike, and matrix spike duplicate.

Section 9. -- Matrix Spike, Matrix Spike Duplicate, Matrix Spike Blank Analysis

In order to evaluate the effects of the sample matrix on the methods used for pesticide/Aroclor analyses, the NYSDEC has prescribed a mixture of pesticide/Aroclor target compounds to be spiked into two aliquots of a sample, and one aliquot of reagent water and analyzed in accordance with the appropriate method.

9.1 A matrix spike and matrix spike duplicate must be extracted and analyzed at least once with every 20 samples of each matrix.

***NOTE**: There is no differentiation between "low" and "medium" soil samples in this method. Therefore only one soil MS/MSD is to be submitted per SDG.*

9.2 The percent recoveries and the relative percent difference between the recoveries of each of the 6 compounds in the matrix spike blank and samples will be calculated and reported by using the following equations:

Equation 12.

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike sample result

SR = Sample result

SA = Spike added

Equation 13.

$$RPD = \frac{|MSR - MSDR|}{1/2(MSR + MSDR)} \times 100$$

Where,

RPD = Relative percent difference

MSR = Matrix spike recovery

MSDR = Matrix spike duplicate recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

9.3 The Laboratory shall report matrix spike and matrix spike duplicate recoveries and percent difference values with the analytical results (see Exhibit B). The limits for matrix spike compound recovery and RPD are given below. As these limits are only advisory, no further action by the Laboratory is required, however, frequent failures to meet the limits for recovery or RPD warrant investigation by the Laboratory, and may result in questions from the NYSDEC.

MATRIX SPIKE RECOVERY AND
RELATIVE PERCENT DIFFERENCE LIMITS

Compound	%Recovery Water	RPD Water	%Recovery Soil	RPD Soil
gamma-BHC (Lindane)	56-123	15	46-127	50
Heptachlor	40-131	20	35-130	31
Aldrin	40-120	22	34-132	43
Dieldrin	52-126	18	31-134	38
Endrin	56-121	21	42-139	45
4,4'-DDT	38-127	27	23-134	50

9.4 The documentation includes Form I PEST for both the MS and MSD analyses, Form III PEST, and chromatograms and a GC/EC data system printout for each analysis.

Section 10. -- Dilution of Samples, Matrix Spikes, Matrix Spike Duplicates, and Matrix Spike Blanks

If the on-column concentration of any sample exceeds the initial calibration range, that sample must be diluted and reanalyzed, as described below. Guidance in performing dilutions and exceptions are given in that paragraph, and reiterated here.

10.1 In order to be quantitated, the detector response (peak area or peak height) of all of the single component analytes must lie between the response of the low and high concentrations in the initial calibration. If the analytes are detected below the CRQL, they are reported as present below the CRQL, and flagged according to the instructions in Exhibit B. If they are detected at a level greater than the high calibration point, the sample must be diluted either to a maximum of 1:100,000 or until the response is within the linear range established during calibration. Guidance in performing dilutions and exceptions to this requirement are given below.

10.1.1 If the response is still above the high calibration point after the dilution of 1:100,000, the Laboratory shall contact the BPSR or Project Director immediately.

10.1.2 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

10.1.3 The dilution factor chosen should keep the response of the largest peak for a target compound in the upper half of the initial calibration range of the instrument.

10.1.4 Do not submit data for more than two analyses, i.e., the original sample extract and one dilution, or, if a screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

10.1.5 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis and note the problem in the SDG Narrative.

10.2 f the response is still above the high calibration point after the dilution of 1:100,000, the Laboratory shall contact the BPSR immediately.

10.3 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

10.4 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

10.5 Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, if the pesticide/Aroclor screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

10.6 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis and note the problem in the SDG Narrative. MSB SAMPLES MUST NEVER BE DILUTED.

Part VI -- Requirements For Non-Pesticides/PCBs Organics By GC

This section outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with all Exhibit D determinations of non-pesticide/PCB organic compounds in water and soil/sediment samples using gas chromatography and various detectors. These QC operations are as follows:

- Method Blank Analysis
- Surrogate Spike Response Monitoring
- Matrix Spike and Matrix Spike Duplicate Analysis
- Matrix Spike Blank Analysis
- Specific QA/QC for Specific Analysis

Section 1 -- Method Blank Analysis

A method blank is a volume of deionized, distilled laboratory water for water samples, or a purified solid matrix for soil/sediment samples, carried through the entire analytical scheme (extraction, concentration, and analysis). For soil/sediment samples, a solid matrix suitable for pesticide analyses must be used if available from EMSL-LV. The method blank volume or weight must be approximately equal to the sample volumes or sample weights being processed.

1.1 Method blank analysis must be performed at the following frequency:

1.1.1 A method blank analysis must be performed once:

- each Sample Delivery Group (SDG), OR
- each 7 calendar day period during which samples in an SDG are received (said period beginning with the receipt of the first sample in that SDG), OR
- each 20 samples in a SDG that are of similar matrix (water or soil) or similar concentration (soil only), OR
- whenever samples are extracted by the same procedure (separatory funnel or continuous extraction),

whichever is most frequent, on each GC system used to analyze samples.

1.2 It is the Laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

1.2.1 For the purposes of this Protocol, an acceptable laboratory method blank must contain less than the Contract Required Quantitation Limit of any single method specified Target Compound (Exhibit C).

1.2.2 If a laboratory method blank exceeds these criteria, the Laboratory must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) MUST be reextracted and reanalyzed at no additional cost to the NYSDEC. The reextraction and reanalysis MUST be performed WITHIN the holding times specified in Exhibit I. The Laboratory Manager, or his designee, must address problems and solutions in the Case Narrative (Exhibit B).

1.3 Documentation

The Laboratory shall report results of method blank analysis using the Organic Analysis Data Sheet (Form I-ORG). In addition, the samples associated with each method blank must be summarized on Form IV-ORG (Method Blank Summary). Detailed instructions for the completion of these forms can be found in Exhibit B.

1.3.1 The Laboratory shall report ALL sample concentration data as UNCORRECTED for blanks.

Section 2 -- Surrogate Spike (SS) Analysis

Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before purging or extraction in order to monitor preparation and analysis of samples.

2.1 Each sample, matrix spike blank, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds prior to extraction. The surrogate spiking compounds specified in the analytical method are used to fortify each sample, matrix spike blank, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocols will not be permitted.

2.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the recovery limits developed by the Laboratory.

2.3 Documentation

The Laboratory shall report surrogate recovery data for the following:

- Method Blank Analysis
- Sample Analysis
- Matrix Spike Blank Analysis
- Matrix Spike/Matrix Spike Duplicate Analyses

The surrogate spike recovery data is summarized on the Surrogate Spike Percent Recovery Summary (Form II-ORG). Detailed instructions for the completion of Form II-ORG are in Exhibit B.

Section 3 -- Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Analysis (MS/MSD/MSB)

In order to evaluate the matrix effect of the sample upon the analytical methodology, the Laboratory must use method specified standard mixes for matrix spike and matrix spike duplicate analyses. These compounds are subject to change depending upon availability and suitability for use as matrix spikes.

3.1 MS/MSD/MSB Frequency of Analysis

A matrix spike, matrix spike duplicate, and matrix spike blank must be performed on those samples so designated by the Contract Lab Sample Information Sheet. If no sample is so designated, the Laboratory shall select a sample for spiking for each group samples of a similar matrix, once:

- each Sample Delivery Group of field samples received, OR
- each 20 field samples in a Sample Delivery Group, OR
- each Sample Delivery Group of samples of a similar concentration level (soils only), OR
- each 7 calendar day period during which samples in a Sample Delivery Group were received (said period beginning with the receipt of the first sample in that Sample Delivery Group),

whichever is most frequent,

UNLESS DIRECTED OTHERWISE BY THE BWAR OR THE PROJECT OFFICER.

3.2 The analytical procedures in Exhibit D, stipulate the amount of matrix spiking solution to be added to the sample aliquots prior to extraction. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike, matrix spike duplicate, and matrix spike blank samples.

3.2.1 Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

3.3 Individual component recoveries of the matrix spike are calculated using Equation 1.

Equation 1.

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Spike Sample Results

SR = Sample Result

SA = Spiked Added from spiking mix

3.4 Relative Percent Difference (RPD)

The Laboratory is required to calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using Equation 2.

Equation 2.

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

where:

RPD = Relative Percent Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

3.5 Documentation

The matrix spike (MS), matrix spike duplicate (MSD), and matrix spike blank (MSB) results (concentrations) for all method specified TCL compounds shall be reported on Form I-ORG (Organic Analysis Data Sheet) and the matrix spike percent recoveries

shall be summarized on Form III-ORG (MS/MSD Recovery). These values will be used by NYSDEC to periodically update existing performance based QC recovery limits.

The results for non-spiked TCL compounds in the matrix spike (MS), matrix spike duplicate (MSD), and matrix spike blank (MSB) analysis shall be reported on Form I-ORG (Organic Analysis Data Sheet) and the percent recovery and the relative percent difference for the matrix spike and matrix spike duplicate shall be summarized on Form III-ORG (MS/MSD Recovery). The RPD data will be used by NYSDEC to evaluate the long term precision of the analytical method. Detailed instructions for the completion of Form III-ORG are in Exhibit B, Section III.

Section 4. -- GC QA/QC Requirements

Paragraph 4 summarizes ongoing QC activities involved with gas chromatography analysis that were detailed in Paragraphs 1, 2, and 3 of this Part, and describes the additional QA/QC procedures required during the gas chromatography analysis that are not covered in Paragraphs 1,2, and 3.

4.1 The Laboratory must perform the following:

4.1.1 Method Blank analysis as per Paragraph 1 of this section.

4.1.2 Spike all standards, samples, blanks, matrix spike blank, matrix spike and matrix spike duplicate samples with the surrogate spike compound as per Paragraph 2 of this section.

4.1.3 Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank analysis as per Paragraph 3 of this section.

4.2 The external standard quantitation method must be used to quantitate all parameters. Before performing any sample analysis, the Laboratory is required to determine the retention time window for each target compound to be determined and the surrogate spike compound. These retention time windows are used to make tentative identification of the target compounds during sample analysis.

4.2.1 Prior to establishing retention time windows, the GC operating conditions (oven temperature and flow rate) must be adjusted as specified in the analytical method.

4.2.2 Establish retention time windows as follows:

4.2.2.1 At the beginning of an analytical sequence make three injections of all target compounds. The concentration of each target analyte should be sufficient to provide a response that is approximately half scale.

4.2.2.2 Verify the retention time shift for the surrogate compound in each analytical standard. The retention time shift between the initial and subsequent standards must be less than a 2.0 percent difference for packed columns (<0.3 percent for capillary column). If this criterion is not met, continue injecting replicate standards to meet criteria.

4.2.2.3 Calculate the standard deviation of the three absolute retention times for each target compound.

4.2.2.4 The standard deviations determined in 4.2.2.3 shall be used to determine the retention time windows for a particular analytical sequence. Apply plus or minus three times the standard deviations in 4.2.2.3 to the retention time of each target analyte determined for the first analysis of the target compound standard in a given analytical sequence. This range of retention times defines the retention time window for the compound of interest for that analytical sequence. Note: By definition, the retention time of a target compound from the first analysis of that compound in the analytical sequence is the center of the retention time window. Do not use the retention time measured in 4.2.2.1 as the center of the retention time window. The experience of the analyst should weigh heavily in the interpretation of chromatograms.

4.2.2.5 In those cases where the retention time window for a particular target compound is less than 0.01 minutes, the Laboratory may substitute whichever of the following formulae apply.

- For packed columns, the retention time window of the particular target compound shall be calculated as $\leq$1% of the initial retention time of the compound in the analytical sequence.

- For wide bore capillary columns (ID greater than 0.32 mm), the retention time window of the particular target compound shall be calculated as ±0.75% of the initial retention time of the compound in the analytical sequence.

- For narrow bore capillary columns (ID less than 0.32 mm), the retention time window of the particular target compound shall be calculated as ±0.15% of the initial retention time of the compound in the analytical sequence.

4.2.2.6 Regardless of whether the retention time windows are calculated by the method in 4.2.2.4 or 4.2.2.5, the retention time windows must be reported as a range of values, not as, for example, 1.51 minutes $\pm$1%.

4.2.2.7 The Laboratory must calculate retention time windows for each target compound on each GC column used at the beginning of the program and whenever a new GC column is installed. The data must be retained by the Laboratory and made available during an on-site laboratory evaluation.

4.3 Primary GC Column Analysis

4.3.1 Primary Analysis establishes whether or not target compounds are present in the sample, and establishes a tentative identification of each compound. Quantitation may be performed on the primary analysis if the analysis meets all of the QC criteria specified for quantitation.

***NOTE**: To determine that no target compounds are present at or above the method detection limit is a form of quantitation.*

4.3.2 Separation should be >25 percent resolution between peaks. This criteria must be considered when determining whether to quantitate on the Primary Analysis or the Confirmation Analysis. When this criteria cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

4.3.3 Evaluation Standard Mixtures

4.3.3.1 Prepare Calibration Standards 3 concentration levels described in Exhibit D. Analyze the three Calibration Standards sequentially at the beginning of each initial calibration sequence.

4.3.3.2 Calculate the Calibration Factor (ratio of the total area to the mass injected) for each compound in Evaluation Standard Mixes using Equation 1.

Equation 1.

$$\text{Calibration Factor} = \frac{\text{Total Area of Peak}}{\text{Mass Injected (in nanograms)}}$$

4.3.3.3 Using the Calibration Factors from 4.3.3.2 above, calculate the percent relative standard deviation (%RSD) for each compound at the three concentration levels using Equation 2. The percent relative standard deviation must be $\leq$10.0 percent.

Equation. 2.

$$\%\ \text{RSD} = \frac{\text{Standard Deviation}}{\overline{CF}} \times 100$$

Where:

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}{n-1}}$$

Where:

x_i = each individual value used to calculate the mean

$\overline{x}$ = the mean of n values

n = the total number of values

4.3.3.4 Suggested Maintenance

Corrective measures may require any one or more of the following remedial actions:

4.3.3.4.1 Packed columns - For instruments with off-column injection; replace the demister trap. Clean and deactivate the glass injection port, insert or replace with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septum). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of packing material if any discoloration is noted, also swab out the inside walls of the column if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described below) and/or repack/replace the column.

4.3.3.4.2 Capillary columns - Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Break off the first few inches, up to one foot, of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

4.3.3.4.3 Metal Injector Body - Turn off the oven and remove the analytical column when oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene; catching the rinsate in the beaker.

Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone and hexane. Reassemble the injector and replace the GC column.

4.4 Sample Analysis (Primary GC Column)

4.4.1 The retention time shift for the surrogate standard must be evaluated after the analysis of each sample. The retention time shift may not exceed a 2.0% difference for packed GC columns between the initial standard analysis and any sample analyzed during the analytical sequence. The percent difference for capillary columns must not exceed 0.3% (Equation 3.).

Equation 3.

$$\text{Percent Difference (\%D)} = \frac{RT_i - RT_s}{RT_i} \times 100$$

Where:

RT_i = absolute retention time of the surrogate standards in the initial standard (Evaluation Standard Mix A).

RT_s = absolute retention time of the surrogate standards in the sample.

4.4.2 If one or more compounds have a response greater than full scale, the extract requires dilution. If the dilution of the extract causes any compounds tentatively identified in the first analysis to be undetectable in the second analysis, then the results of both analyses shall be reported on separate Forms I-ORG, according to the instructions in Exhibit B. For dilutions greater than 10-fold, an additional analysis at a concentration 10 times the maximum dilution, must be run to identify and quantitate lower concentration analytes.

4.5 Confirmation Analysis

4.5.1 Confirmation Analysis is to confirm the presence of all compounds tentatively identified in the Primary Analysis. Therefore, the only standards that are required are the Calibration Standard mixes and standards of all compounds to be confirmed. The analytical sequence is, therefore, modified to fit each case. Quantitation may be performed on the confirmation analysis.

4.6 Instrument Detection Limit Determination

Before any field samples are analyzed under this protocol, the instrument detection limits (in µg/L must be determined for each instrument used, within 30 days of the start of the analysis of samples under this protocol and at least quarterly (every 3 calendar months) thereafter, and must meet the levels specified in Exhibit C.

4.8 Documentation

See Exhibit B for complete instructions for the completion of all required forms and the Deliverable Index for all reporting and deliverables requirements.

Part VII -- Requirements For Inorganics

The quality assurance/quality control (QA/QC) procedures defined herein must be used by the Laboratory when performing the methods specified in Exhibit D, CLP, Inorganics. When additional QA/QC procedures are specified in the methods in Exhibit D, CLP, Inorganics, the Laboratory must also follow these procedures.

***NOTE**: The cost of performing all QA/QC procedures specified in this protocol is included in the price of performing the individual analyses, except for duplicate, spike and laboratory control sample analyses, which shall be considered separate sample analyses.*

The purpose of this document is to provide a uniform set of procedures for the analysis of inorganic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The primary function of the QA/QC program is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation (Exhibit D). Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Laboratory is required to participate in the Environmental Laboratory Accreditation Program run by the New York State Department of Health. The Laboratory can expect to analyze at least two samples per year.

The Laboratory must perform and report to the Bureau of Program Services and Research as specified in Exhibit B, quarterly verification of instrument detection limits (IDL) by the method specified in Exhibit E, by type and model for each instrument used on this protocol. All IDLs must meet the CRDLs specified in Exhibit C. For ICP methods, the Laboratory must also report, as specified in Exhibit B, linearity range verification, all interelement correction factors, wavelengths used, and integration times.

In this Exhibit, as well as other places within this Protocol, the term "analytical sample" is used in discussing the required frequency or placement of certain QA/QC measurements. The term "analytical sample" is defined in the glossary, Exhibit G. As the term is used, analytical sample includes all field samples, including Performance Evaluation samples, received from an external source, but it also includes all required QA/QC samples (matrix spikes, analytical/post-digestion spikes, duplicates, serial dilutions, LCS, ICS, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, ICV/ICB, CCV/CCB). A "frequency of 10%" means once every 10 analytical samples.

***NOTE**: Calibration verification samples (ICV/CCV) and calibration verification blanks (ICB/CCB) are not counted as analytical samples when determining 10% frequency.*

In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their QA/QC analysis must be analyzed under the same operating and procedural conditions.

If any QC measurement fails to meet contract criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in Exhibit E.

The Laboratory must report all QC data in the exact format specified in Exhibits B and H.

Sensitivity, instrumental detection limits (IDL's), precision, linear dynamic range and interference effects must be established for each analyte on a particular instrument. All reported measurements must be within the instrumental linear ranges. The analyst must maintain quality control data confirming instrument performance and analytical results. In addition, the Laboratory shall establish a quality assurance program with the objective of providing sound analytical chemical measurements. This program shall incorporate the quality control procedures, any necessary corrective action, and all documentation required during data collection as well as the quality assessment measures performed by management to ensure acceptable data production. As evidence of such a program, the Laboratory shall prepare a written Quality Assurance Plan (QAPP) (see Section III) which describes the procedures that are implemented to achieve the following:

Maintain data integrity, validity, and usability.

Ensure that analytical measurement systems are maintained in an acceptable state of stability and reproducibility.

Detect problems through data assessment and establishes corrective action procedures which keep the analytical process reliable.

Document all aspects of the measurement process in order to provide data which are technically sound and legally defensible.

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the protocol. The following QA/QC operations must be performed as described in this Exhibit.

1. Instrument Calibration

2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

3. CRDL Standards for AA (CRA) and ICP (CRI)

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses.

5. ICP Interference Check Sample (ICS) Analyses

6. Spike Sample Analysis (S)

7. Duplicate Sample Analysis (D)

8. Laboratory Control Sample (LCS) Analysis

9. ICP Serial Dilution Analysis (L)

10. Instrument Detection Limit (IDL) Determination

11. Interelement Corrections for ICP (ICP)

12. Linear Range Analysis (LRA)

13. Furnace AA QC Analyses

Section 1. -- Instrument Calibration

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D, Part V. Instruments must be calibrated daily or once every 24 hours, and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Date and time of preparation and analysis must be given in the raw data.

Calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the CRDL except for mercury. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required 4-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. Results for these standards must be within ±5% of the true value. Each standards concentration and the calculations to show that ±5% criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary.

The ±5% criteria does not apply to the atomic absorption calibration standard at the CRDL.

Calibration standards for AA procedures must be prepared as described in Exhibit D, CLP, Inorganics.

Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification check. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D, CLP, Inorganics. One cyanide calibration standard must be at the CRDL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least two standards must be used for ICP calibration. One of the standards must be a blank.

Section 2. -- Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

2.1 Initial Calibration Verification (ICV)

Immediately after each of the ICP, AA and cyanide systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the control limits of Table 1 - Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used for analysis. For CN, the initial calibration verification standard must be distilled. The Initial Calibration Verification for CN serves as a Laboratory Control Sample; thus it must be distilled with the batch of samples analyzed in association with that ICV. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV. The values for the initial and subsequent continuing calibration verifications shall be recorded on FORM II-IN for ICP, AA, and cyanide analyses, as indicated.

2.2 Continuing Calibration Verification (CCV)

To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard must also be analyzed for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near the mid-range levels of the calibration curve:

1. EPA Solutions

2. NBS SRM 1643a

3. A laboratory-prepared standard solution

Table 1.
INITIAL AND CONTINUING CALIBRATION VERIFICATION CONTROL LIMITS FOR INORGANIC ANALYSES

Analytical Method	Inorganic Species	% of True Value (EPA Set) Low Limit	High Limit
ICP/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115

The same continuing calibration standard must be used throughout the analysis runs for each Sample Delivery Group of samples received.

Each CCV analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it as well as the difference in time between the CCV and the analytical sample immediately preceding it may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

If the deviation of the continuing calibration verification is greater than the control limits specified in Table 1 - Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses, the analysis must be stopped, the problem corrected, the instrument must be recalibrated, the calibration verified and the reanalysis of the preceding 10 analytical samples or all analytical samples analyzed since the last good calibration verification must be performed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on FORM II-IN for ICP, AA and cyanide as indicated.

Section 3. -- CRDL Standards for ICP (CRI) and AA (CRA)

To verify the linearity near the CRDL for ICP analysis, the Laboratory must analyze an ICP standard (CRI) at two times the CRDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run by ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na and K.

To verify linearity near the CRDL for AA Analysis, the Laboratory must analyze an AA standard (CRA) at the CRDL or the IDL, whichever is greater, at the beginning of each sample analysis run, but not before the Initial Calibration Verification.

Specific acceptance criteria for the two standards will be set by NYSDEC in the future. In the interim, the Laboratory must analyze and report these Standards on FORM II (PART 2)-IN.

Section 4. -- Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses

4.1 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample.

***NOTE**: A CCB must be run after the last CCV that was run after the last analytical sample of the run.*

The results for the calibration blanks shall be recorded on FORM III-IN for ICP, AA and cyanide analyses, as indicated. If the magnitude (absolute value) of the calibration blank results exceeds the IDL, the result must be so reported in µg/L on FORM III-IN, otherwise report as IDL-U. If the absolute value blank result exceeds the CRDL (Exhibit C), terminate analysis, correct the problem, recalibrate and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last good calibration blank.

4.2 Preparation Blank (PB) Analysis

At least one preparation blank (or reagent blank), consisting of deionized, distilled water processed through each sample preparation and analysis procedure (See Exhibit D, Part V), must be prepared and analyzed with every Sample Delivery Group, or with each batch[1] of samples digested, whichever is more frequent.

The first batch of samples in an SDG is to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. (see FORM III-IN). Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

This blank is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

1) If the absolute value of the concentration of the blank is less than or equal to the Contract Required Detection Limit (Exhibit C), no corrective action is required.

2) If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's

concentration less than 10x the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.

3) If the concentration of the blank is below the negative CRDL, then all samples reported below 10x CRDL associated with the blank must be redigested and reanalyzed.

The values for the preparation blank must be recorded in µg/L for aqueous samples and in mg/Kg for solid samples on FORM III-IN for ICP, AA, and cyanide analyses.

Section 5. -- ICP Interference Check Sample (ICS) Analysis

To verify interelement and background correction factors, the Laboratory must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The ICP Interference Check Samples must be obtained from EPA (EMSL/LV) if available and analyzed according to the instructions supplied with the ICS.

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of ±20% of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last good ICS. If true values for analytes contained in the ICS and analyzed by ICP are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination must be made during an analytical run where the results for the previously supplied EPA ICS met all protocol specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (.e., until the solution is exhausted).

If the ICP Interference Check Samples is not available from EPA, independent ICP Check Samples must be prepared with interferent and analyte concentrations at the levels specified in Table 2-Interferent and Analyte Elemental Concentrations Used for ICP Interference Check Sample. The mean value and standard deviation must be established by initially analyzing the Check Samples at least five times repetitively for each parameter on FORM IV-IN. Results must fall within the control limit of ±20% of the established mean value. The mean and standard deviation must be reported in the raw data. Results from the Interference Check Sample analyses must be recorded on FORM IV-IN for all ICP parameters.

TABLE 2.
INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

Section 6. -- Spiked Sample Analysis

The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e. prior to the addition of other reagents) and prior to any distillation steps (i.e., CN^-). NYSDEC will designate, on the Contract Lab Sample Information Sheet, the sample to be used for spike and duplicate analyses. If no sample from an SDG is so designated, then the Laboratory is to select one. At least one spiked sample analysis must be performed on each group of samples of a similar matrix type (i.e. water, soil) and concentration (i.e. low, medium) or for each Sample Delivery Group, whichever is more frequent.[2]

If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see Paragraph 7, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. NYSDEC may require that a specific sample be used for the spike sample analysis.

The analyte spike must be added in the amount given in Table 3 - Spiking Levels for Spike Sample Analysis, for each element analyzed. If two analytical methods are used to obtain the reported values for the same element within a sample Delivery Group (i.e. ICP, AA, GFAA), spike samples must be run by each method used.

If the spike recovery is not within the limits of 75 - 125%, the data of all samples received associated with that spiked sample must be flagged with the letter "N" on

[2] NYSDEC may require additional spike sample analysis, upon BTSR request, for which the Laboratory will be paid.

FORMS I-IN and V-IN. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75 - 125% recovery criteria.

For flame AA, ICP, and CN analyses, when the pre-digestion/pre-distillation spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added, a post-digestion/post-distillation spike must be performed for those elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x CRDL, whichever is greater. Results of the post-digestion/post-distillation spike must be reported on FORM V (PART 2)-IN.

***NOTE**: No post digestion spike is required for mercury.*

In the instance where there is more than one spike sample per matrix and concentration per method per SDG, if one spike sample recovery is not within protocol criteria, flag all the samples of the same matrix, level, and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

$$\% \text{ Recovery} = \frac{(SSR-SR)}{SA} \times 100$$

Where:

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating % Recovery. The spike sample results, sample results and % Recovery (positive or negative) must be reported on FORM V-IN for ICP, AA and cyanide analyses, as indicated.

The units for reporting spike sample results will be identical to those used for reporting sample results in FORM I-IN (i.e., µg/L for aqueous and mg/Kg dry weight basis for solid).

TABLE 3. - SPIKING LEVELS FOR SPIKED SAMPLE ANALYSIS.

	For ICP/AA		For Furnace AA		Other(1)
Element	Water (µg/L)	Soil[2] (mg/Kg)	Water (µg/L)	Soil (mg/Kg)	
Aluminum	2,000	*			
Antimony	500	100	100	20	
Arsenic	2,000	400	40	40	
Barium	2,000	400			
Beryllium	50	10			
Cadmium	50	10	5	1	
Calcium	*	*			
Chromium	200	40			
Cobalt	500	100			
Copper	250	50			
Iron	1,000	*			
Lead	500	100	20	4	
Magnesium	*	*			
Manganese	500	100			
Mercury					1
Nickel	500	100			
Potassium	*	*			
Selenium	2,000	400	10	2	
Silver	50	10			
Sodium	*	*	*		
Thallium	2,000	400	50	10	
Vanadium	500	100			
Zinc	500	100			
Cyanide					100[3]

* No spike required. **NOTE**: Elements without spike levels and not designated with an asterisk, must be spiked at appropriate levels.

(1) Spiking level reported is for both water and soil/sediment matrices

(2) The levels shown indicate concentrations in the final digestate of the spiked sample (100 mL for mercury and 200 mL for all other metals) when the wet weight of 1 gram (for ICP, Furnace, and Flame AA), or 0.2 grams (for mercury) of sample is taken for analysis. Adjustment must be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values. Appropriate adjustment must be made for microwave digestion procedure where 0.5 grams of sample or 50.0 mL (45.0 mL of sample plus 5.0 mL of acid) of aqueous sample are required for analysis.

(3) The level shown indicates the amount of cyanide that must be added to the original (undistilled) sample. For instance, 100 µg must be added per each Liter of aqueous sample. If the sample volume is 500 mL, then 50 µg of cyanide must be added. If the volume is 50 mL, then 5 µg of cyanide must be added. For soil samples, 25 µg of cyanide must be added per each gram of solid sample taken for analysis. The spiking level is dependent on the weight of the sample taken and the final distillate volume. If one gram of sample is taken for analysis, and the final distillate volume is 250 mL, then the distillate must contain cyanide at a concentration of 100 µg/L. If five grams of sample are taken, then the distillate must contain cyanide at a concentration of 500 µg/L. Assuming a sample of one gram, the manual and semi-automated colorimetric methods call for a cyanide concentration of 50 µg per the 500 mL mixture of the sample, reagents, and water before distillation. The final distillate, in this case, contains cyanide at a concentration of 100 µg/L. For the midi-distillation method, a cyanide concentration of 25 µg must be added into the 50 mL mixture of sample, reagents, and water before distillation. This yields a cyanide concentration of 500 µg/L in the final distillate of 50 mL.

Section 7. -- Duplicate Sample Analysis

NYSDEC will designate, on the Contract Lab Sample Information Sheet, the sample to be used for spike and duplicate analyses. If no sample from a SDG is so designated, then the Laboratory is to select one. One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Duplicates cannot be averaged for reporting on FORM I-IN.

Duplicate sample analyses are required for percent solids. Samples identified as field blanks cannot be used for duplicate sample analysis. NYSDEC may require that a specific sample be used for duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a Sample Delivery Group (i.e., ICP, GFAA), duplicate samples must be run by each method used.

The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where:

RPD = Relative Percent Difference

S = First Sample Value (original)

D = Second Sample Value (duplicate)

The results of the duplicate sample analyses must be reported on FORM VI-IN in µg/L for aqueous samples and mg/Kg dry weight basis for solid original and duplicate samples. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x CRQL (Exhibit C). A control limit of (±) the CRDL must be used for sample values less than 5x CRDL, and the absolute value of the control limit (CRDL) must be entered in the "Control Limit" column on FORM VI-IN.

If one result is above the 5x CRDL level and the other is below, use the ±CRQL criteria. If both sample values are less than the IDL, the RPD is not calculated on FORM VI-IN. For solid sample or duplicate results <5x CRDL, enter the absolute value of the CRDL, corrected for sample weight and percent solids, in the "Control Limit" column.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on FORMs I-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within protocol criteria, flag all samples of the same matrix, concentration, and method in the SDG. The percent difference data will be used by NYSDEC to evaluate the long-term precision of the methods for each parameter. Specific control limits for each element will be added to FORM VI-IN at a later date based on these precision results.

Section 8. -- Laboratory Control Sample (LCS) Analysis

Aqueous and solid Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC

procedures employed for the NYSDEC samples received. The aqueous LCS solution must be obtained from EPA (if unavailable, the Initial Calibration Verification Solutions may be used). One aqueous LCS must be prepared and analyzed for every group of aqueous samples in the Sample Delivery Group, or for each batch of aqueous samples digested, whichever is more frequent. An aqueous LCS is not required for mercury and cyanide analysis.

The EPA-provided solid LCS must be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the EPA solid LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used. One solid LCS must be prepared and analyzed for every group of solid samples in a Sample Delivery Group, or for each batch of samples digested, whichever is more frequent.

All LCS results and percent recovery (%R) will be reported on FORM VII-IN. If the percent recovery for the aqueous LCS falls outside the control limits of 80 - 120% (exception: Ag and Sb), the analyses must be terminated, the problem corrected, and the previous samples associated with the LCS redigested and reanalyzed.

If the results for the solid LCS fall outside the control limits established by EPA, the analyses must be terminated, the problem corrected, and the previous samples associated with the LCS redigested and reanalyzed.

All redigestion and reanalysis must be performed within the holding times specified in Exhibit I.

Section 9. -- ICP Serial Dilution Analysis (L)

Prior to reporting concentration data for the analyte elements, the Laboratory must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil and concentration) (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), an analysis of a 5-fold dilution must agree within 10% of the original determination. If the dilution analysis for one or more analytes is not within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with the serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

The percent differences for each component are calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

Where:

I = Initial Sample Result

S = Serial Dilution Result (Instrument Reading x 5)

In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within protocol criteria, flag all the samples of the same matrix and concentration in the Sample Delivery Group. Serial dilution results and "E" flags must be reported on FORM IX-IN.

Section 10. -- Instrument Detection Limit (IDL) Determination

Before any field samples are analyzed under this Protocol, the instrument detection limits (in µg/L) must be determined for each instrument used, within 30 days of the start of the analysis of samples under this Protocol and at least semiannually (every 6 calendar months), and must meet the levels specified in Exhibit C, Superfund-TCL.

The Instrument Detection Limits (in µg/L) shall be determined by multiplying by t_{n-1}, the standard deviation obtained on three days from the analysis of a minimum of seven replicate analyses of a standard solution (each analyte in reagent water) at a concentration 3x - 5x IDL on each day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples. The standard deviation (s_c) at this concentration is then calculated with n-1 degrees of freedom. The instrument detection limits shall be calculated as follows:

$$IDL = t_{n-1} \times s_c$$

where t_{n-1} is the Students t-Test value for a 99% confidence level at the n-1 level and n is the number of replicates. For twenty-one replicates, $t_{n-1} = 2.528$.

The semiannually determined IDL for an instrument must always be used as the IDL for that instrument during the following six month time period. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of that six month period.

IDLs must be reported on FORM XI-IN for each instrument used and submitted with each data package. If multiple AA instruments are used for the analysis of an element within a Sample Delivery Group, the highest IDL for the AAs must be used for reporting concentration values for that Sample Delivery Group. The same reporting procedure must be used for multiple ICPs.

Section 11. -- Interelement Corrections for ICP

Before any field samples are analyzed under this protocol, the ICP interelement correction factors must be determined within six months of the start of the analysis of samples under this Protocol and at least annually thereafter. Correction factors for

spectral interference due to Al, Ca, Fe, and Mg must be determined at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use. Results from interelement correction factors determination must be reported on FORM XII (PART I)-IN and FORM XII(PART 2)-IN for all ICP parameters and submitted with each data package.

Section 12. -- Linear Range Analysis (LRA)

For all ICP analysis, a linear range verification check standard must be analyzed and reported semiannually (every 6 calendar months) for each element on FORM XII-IN. The standard must be analyzed during a routine analytical run performed under this Protocol. The analytically determined concentration of this standard must be within ±5% of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under this Protocol without dilution of the analytical sample.

Section 13. -- Furnace Atomic Absorption (AA) QC Analyses

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1 - Furnace AA Analysis Scheme (MSA Tree) will be required for quantitation. (These procedures do not replace those in Exhibit D, CLP, Inorganics of this Protocol, but supplement the guidance provided therein.)

13.1 All furnace analyses must fall within the calibration range. In addition, all analyses, except during full Methods of Standard Addition (MSA), will require duplicate injections. The absorbance or concentration of each injection must be reported in the raw data as well as the average absorbance or concentration values and the relative standard deviation (RSD) or coefficient of variation (CV). Average concentration values are used for reporting purposes. The Laboratory must be consistent per method and SDG in choosing absorbance or concentration to evaluate which route is to be followed in the MSA Tree. The Laboratory must also indicate which of the two is being used if both absorbance and concentration are reported in the raw data. For MSA analysis, the absorbance of each injection must be included in the raw data. A maximum of 10 full sample analyses to a maximum of 20 injections may be performed between each consecutive calibration verifications and blanks. For concentrations greater than the CRDL, the duplicate injection readings must agree within 20% RSD or CV, or the analytical sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value reported on FORM I-IN with an "M". The "M" flag is required for the analytical spike as well as the sample. If the analytical spike for a sample requires an "M" flag, the flag must be reported on FORM I-IN for that sample.

13.2 All furnace analyses for each analytical sample, including those requiring an "M" flag, will require at least an analytical spike to determine if the MSA will be required for quantitation. The analytical spike[4] will be required to be at a concentration (in the sample aliquot) 2x CRDL (except for lead which must be at 20 µg/L). This requirement for an analytical spike will include the LCS and the preparation blank. (The LCS must be quantitated from the calibration curve and corrective action, if needed,

taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results.) If the preparation blank analytical spike recovery is out of control (85 - 115%), the spiking solution must be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control, correct the problem and reanalyze all analytical samples associated with that blank. An analytical spike is not required on the pre-digestion spike sample.

The analytical spike of a sample must be run immediately after that sample. The percent recovery (%R) of the "spike", calculated by the same formula as Spike Sample Analyses (see Paragraph 6), will then determine how the sample will be quantitated, as follows:

13.2.1 If the analytical spike recovery is less than 40%, the sample must be diluted and rerun. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the analytical spike recovery is still <40%, report data and flag with an "E" to indicate interference problems.

13.2.2 If the analytical spike recovery is greater than or equal to 40% and the sample absorbance or concentration is less than 50% of the "spike"[(5)], report the sample results to the IDL. If the analytical spike recovery is less than 85% or greater than 115%, flag the result with a "W".

13.2.3 If the sample absorbance or concentration is greater than or equal to 50% of the analytical spike, and the analytical spike recovery is between 85% and 115%, the sample must be quantitated directly from the calibration curve and reported down to the IDL.

13.2.4 If the sample absorbance or concentration is greater than or equal to 50% of the analytical spike, and the analytical spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.

13.3 The following procedures will be incorporated into MSA analyses.

13.3.1 Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

13.3.2 The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation.

Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

13.3.3 For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.

13.3.4 Spikes must be prepared such that:

13.3.4.1 Spike 1 is approximately 50% of the sample absorbance or concentration.

13.3.4.2 Spike 2 is approximately 100% of the sample absorbance or concentration.

13.3.4.3 Spike 3 is approximately 150% of the sample absorbance or concentration.

13.3.5 The data for each MSA analysis must be clearly identified in the raw data documentation (using added concentration as the x-variable and absorbance as the y-variable) along with the slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data, and the results reported on FORM VIII-IN. Reported values obtained by MSA must be flagged on the data sheet (FORM I-IN) with the letter "S" if the correlation coefficient is greater than or equal to 0.995.

13.3.6 If the correlation coefficient (r) for a particular analysis is less than 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still less than 0.995, report the results on FORM I-IN from the run with the best "r" and flag the result with a "+" on FORM VIII-IN and FORM I-IN.

Section 14. -- Footnotes

1 A group of samples prepared at the same time.

2 NYSDEC may require additional spike sample analysis, upon request, for which the Laboratory will be paid.

3 NYSDEC may require additional duplicate sample analyses, upon request, for which the Laboratory will be paid.

4 Analytical spikes are post-digestion spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume changing the spike samples by addition of deionized water to the unspiked sample aliquot. The volume of the spiking solution added must not exceed 10% of the analytical sample volume; this requirement also applies to MSA spikes.

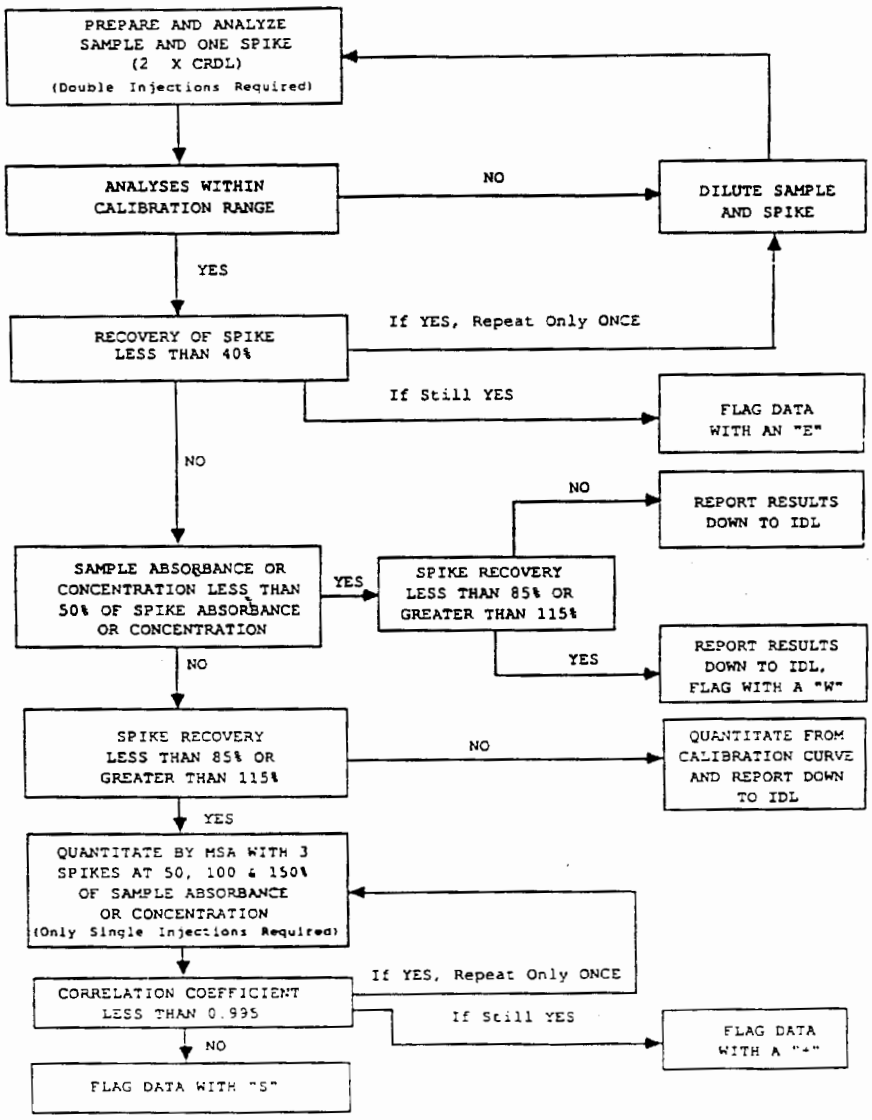
5 "Spike" is defined as [absorbance or concentration of spike sample] minus [absorbance or concentration of the sample].

$$\% \text{ Recovery} = \frac{(SSR-SR)}{SA} \times 100$$

Where:

SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Figure 1 - Furnace Atomic Absorption Analysis Scheme



Part VIII -- Requirements For Wet-Chemical Analysis

For manual colorimetric analytical procedures an initial five standard calibration curve must be generated every three months, with a reagent blank and a continuing calibration standard being run with every sample batch. If the concentration of the continuing calibration standard, as calculated from the initial calibration curve, exceeds ±10% of the theoretical concentration then that batch of samples must be rerun. If the rerun still exceeds ±10% then the system should be considered out of control and a new initial calibration curve must be generated.

Part IX -- Requirements For Low Concentration Volatile Organics By Gc/Ms (Methods CLP-Low Organics, 524.2, 8260)

This Part outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with GC/MS determinations of low concentration volatile organic compounds in water. This section is not intended as a comprehensive quality control document, but rather as a guide to the specific QC operations that must be considered for volatile analyses. At a minimum, the Laboratory is expected to address these operations in preparing the Quality Assurance Program Plan and QA/QC Standard Operating Procedures discussed in Section II. **NOTE**: When there is a conflict between the QA/QC requirements in a volatile organic analysis method in Exhibit D and those specified here in Exhibit E. Exhibit E requirements must be followed.

These QC operations include the following:

- GC/MS Mass Calibration and Ion Abundance Pattern
- GC/MS Initial and Continuing Calibration
- Stability of Internal Standard Response and Retention Times
- Method Blank Analysis
- Holding Blank Analysis
- System Monitoring Compound Recoveries
- Matrix Spike and Matrix Spike Duplicate Analysis
- Matrix Spike Blank Analysis
- Dilution of Samples, Matrix Spikes, and Matrix Spike Duplicates

Not discussed in this section are the requirements for quality assurance of the data reporting aspects of volatile analyses which are described in general terms in Section II and III of this exhibit.

Section 1 -- GC/MS Mass Calibration and Ion Abundance Patterns

Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that a given GC/MS system meets the instrument performance criteria specified in Paragraph 1.1. The purpose of this instrument performance check is to assure correct mass calibration, mass resolution, and mass transmission. This is accomplished through the analysis of p-Bromofluorobenzene (BFB).

Definition: The twelve (12) hour time period for GC/MS mass calibration and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the BFB analysis that the Laboratory submits as documentation of a compliant instrument performance check. The time period ends after twelve (12) hours has elapsed according to the system clock.

1.1 p-Bromofluorobenzene (BFB)

1.1.1 Each GC/MS system used for the analysis of volatile TCL compounds must be mass calibrated to meet the ion abundance criteria listed in Table 1 for a maximum of a 50 nanogram injection of BFB. Alternately, add 50 ng of BFB solution to 5.0 mL of reagent water and analyze according to Exhibit D. BFB shall not be analyzed simultaneously with any calibration standards or blanks. This criterion must be demonstrated daily or for each twelve (12) hour time period, whichever is more frequent. If required, background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the Protocol specifications are unacceptable.

***NOTE**: All instrument conditions must be identical to those used in sample analysis, except that a different temperature program may be used.*

1.1.2 BFB criteria MUST be met before any standards, samples, or blanks are analyzed. Any samples analyzed when mass calibration criteria have not been met may require reanalysis at no cost to the NYSDEC.

1.1.3 Whenever the Laboratory takes corrective action which may change or affect the mass calibration criteria for BFB (e.g., ion source cleaning or repair, etc.), the mass calibration must be verified irrespective of the 12-hour requirements.

TABLE 1. - BFB KEY IONS AND ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15.0 - 40.0 percent of the base peak
75	30.0 - 60.0 percent of the base peak
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of the base peak
173	less than 2.0 percent of mass 174
174	greater than 50.0 percent of the base peak
175	5.0 - 9.0 percent of mass 174
176	greater than 95.0 percent but less than 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

1.2 Documentation

Documentation of the calibration must be provided in the form of a bar graph plot and as a mass listing.

1.2.1 The Laboratory shall complete a Form V-VOA (Volatile Organic Instrument Performance Check) each time an analytical system is mass calibrated. In addition, all samples, standards, blanks, matrix spikes, matrix spike

duplicates, and matrix spike blanks analyzed during a particular instrument performance check must be summarized on the bottom of the appropriate Form V. Detailed instructions for the completion of Form V are found in Exhibit B, Section III.

Section 2 -- GC/MS Initial Calibration for Target Compounds and System Monitoring Compounds

Prior to the analysis of samples and required blanks and after instrument performance criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations, analyzed consecutively under the same BFB tune, to determine the linearity of response utilizing standards for TCL compounds as specified in Exhibit C for the particular analytical method employed.

2.1 Prepare five aqueous initial calibration standard solutions containing all of the purgeable target compounds and the system monitoring compounds at the 1.0, 2.0, 5.0, 10 and 25 µg/L levels, except the ketones which are at the 5.0, 10, 25, 50, and 125 µg/L levels. The preparation procedure for the aqueous calibration standard solutions is listed in Table 2. Add 10 µL of the internal standard solution to each aqueous standard. Analyze each calibration standard. If a compound saturates at the highest standard concentration, and the GC/MS system is calibrated to achieve a detection sensitivity of no less than 1.0 µg/L, the Laboratory must document it in the SDG Narrative and attach a quantitation report and RIC. In this instance, the Laboratory must calculate the results based on a four-point initial calibration for the specific compound that saturates. Secondary ion quantitation is only allowed when there are sample interferences with the primary quantitation ion. If secondary ion quantitation is used, calculate a relative response factor using the are response from the most intense secondary ion which is free of sample interferences and document the reasons for the use of the secondary ion in the SDG Narrative.

TABLE 2

VOL OF WORKING STANDARD (µL added to 25 mL)	FINAL CONC OF AQUEOUS STANDARD FOR NON-KETONES (µg/L)	FINAL CONC OF AQUEOUS STANDARD FOR KETONES (µg/L)
5	1	5
10	2	10
25	5	25
50	10	50
125	25	125

2.2 The NYSDEC has specified both the concentration levels for initial calibration and has also specified the specific internal standard to be used on a compound-by-compound basis for quantitation (see Tables 3 through 4) Establishment of standard calibration procedures is necessary and deviations by the Laboratory will not be allowed.

2.3 Analyze each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including all Protocol required system monitoring compounds. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time. Late eluting compounds usually will have much better agreement.

Using Tables 2 through 4 and Equation 1, calculate the relative response factors (RRF) for each compound at each concentration level.

Equation 1

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the specific internal standards from Table 2.

C_{is} = Concentration of the internal standard (µg/mL).

C_x = Concentration of the compound to be measured (µg/mL).

TABLE 3
VOLATILE TARGET COMPOUNDS AND SYSTEM MONITORING COMPOUNDS WITH CORRESPONDING METHODS CLP-LOW ORGANIC VOLATILES AND 524.2 INTERNAL STANDARDS FOR QUANTITATION

1.4-DIFLUOROBENZENE	CHLOROBENZENE-d_5	1.4-DICHLOROBENZENE-d_4
Acetone	Benzene	Bromoform
Brorochloromethane	Bromodichloromethane	1,2-Dibromo-3-chloropropane
Bromomethane	Carbon tetrachloride	1,2-Dichlorobenzene
2-Butanone	Chlorobenzene	1,3-Dichlorobenzene
Carbon disulfide	Dibromochloromethane	1,4-Dichlorobenzene
Chloroethane	1,2-Dibromoethane	
Chloroform	1,2-Dichloropropane	
Chloromethane	cis-1,3-Dichloropropene	
1,1-Dichloroethane	trans-1,3-Dichloropropene	
1,2-Dichloroethane	Ethylbenzene	
1,1-Dichloroethene	2-Hexanone	
cis-1,2-Dichloroethene	4-Methyl-2-pentanone	
trans-1,2-Dichloroethene	Styrene	
Methylene chloride	1,1,2,2-Tetrachloroethane	
Vinyl chloride	Tetrachloroethene	
4-Bromofluorobenzene (smc)	Toluene	
1,2-Dichloroethane-d_4 (smc)	1,1,1-Trichloroethane	
	1,1,2-Trichloroethane	
	Trichloroethene	
	Xylenes (total)	
	Toluene-d_8 (smc)	

TABLE 4 - VOLATILE INTERNAL STANDARDS WITH CORRESPONDING METHOD 8260 ANALYTES ASSIGNED FOR QUANTITATION

Pentafluorobenzene	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloromethane		2-Hexanone
Bromomethane	Carbon tetrachloride	4-Methyl-2-pentanone
Vinyl chloride		Tetrachloroethene
Chloroethane	Bromodichloromethane	1,1,2,2-Tetrachloroethane
Methylene chloride	1,2-Dichloropropane	Toluene
Acetone	trans-1,3-Dichloropropene	Chlorobenzene
Carbon disulfide	Trichloroethene	Ethylbenzene
1,1-Dichloroethene		Styrene
1,1-Dichloroethane	1,1,2-Trichloroethane	Xylenes (Total)
cis-1,2-Dichloroethene	Benzene	Bromofluorobenzene
trans-1,2-Dichloroethene	cis-1,3-Dichloropropene	(surr)
Chloroform	Bromoform	Toluene-d_8 (surr)
2,2-Dichloropropane	2-Butanone	Ethyl methacrylate
Dichlorodifluoromethane	2-Chloroethyl vinyl ether	1,2,3-Trichloropropane
Acrolein	Dibromomethane	Dibromochloromethane
Acrylonitrile	1,4-Dichloro-2-butene	
Iodomethane	1,2-Dichloroethane	
Trichlorofluoromethane	1,2-Dichloroethane-d_4	
1,1,1-Trichloroethane	(surr)	
Vinyl acetate		

(surr) = surrogate compound

2.4 The calibration of the GC/MS is evaluated on the basis of the magnitude and stability of the relative response factors of each target compound and system monitoring compound.

2.4.1 Using the relative response factors (RRF) from the initial calibration, calculate the percent relative standard deviations (%RSD) for all calibration compounds using Equation 2 below.

Equation. 2

$$\%RSD = \frac{\text{Standard deviation}}{\text{mean}} \times 100$$

Where:

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}{n-1}}$$

Where:

x_i = each individual value used to calculate the mean

$\overline{x}$ = the mean of n values

n = the total number of values

2.4.2 The response factors of the compounds listed below (Table 5.) must meet the minimum RRF criteria at each concentration level and maximum %RSD criteria for the initial calibration, with allowance made for up to two volatile compounds. However, the RRFs for those two compounds must be greater than or equal to 0.010, and the %RSD of those two compounds must be less than or equal to 40.0% for the initial calibration to be acceptable.

2.4.3 Note that the following compounds have a Maximum %RSD of 100.%, and a Maximum %Difference of 100.%. These compounds must also meet a minimum RRF criteria of 0.010:

Acetone	1,2-Dichloropropane
2-Butanone	2-Hexanone
Carbon disulfide	Methylene chloride
Chloroethane	4-Methyl-2-pentanone
Chloromethane	Toluene-d_8
1,2-Dichloroethene (total)	1,2-Dichloroethane-d_4

2.4.4 A check of the calibration curve must be performed once every 12 hours (see Paragraph 1. for the definition of the twelve hour time period). Check the relative response factors of those compounds for which RRF values have been established. If these criteria are met, the relative response factors for all compounds are calculated and reported. A percent difference of the daily relative response factor (12 hour) compared to the average relative response factor from the initial curve is calculated. Calculate the percent difference for each compound and compare with the maximum percent difference criteria listed above. For negative percent difference values, the value must be greater than or equal to -25.0%, but less than 0%. As with the initial calibration, up to two volatile compounds in Table 2 may fail to meet the minimum RRF or maximum %D criteria, but the RRFs of those two compounds must be greater than or equal to 0.010, and the percent differences must be less than or equal to 40.0% for the continuing calibration to be acceptable.

2.4.5 Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 0.50 minutes (30 seconds) from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard

changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is required.

2.5 Each GC/MS system must be calibrated upon award of the contract, whenever the Laboratory takes corrective action which may change or affect the initial calibration criteria (i.e., ion source cleaning or repair, column removal or replacement, etc.), or if the continuing calibration acceptance criteria have not been met.

2.6 If time remains in the 12 hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard, if the initial calibration meets the calibration acceptance criteria above. A method blank is necessary. Quantify all sample results against the initial calibration standard that is the same concentration as the continuing calibration standard (50 µg/L).

2.7 If time does not remain in the 12-hour period beginning with the injection of the instrument performance check solution, a new injection of the instrument performance check solution must be made. If the new injection meets the ion abundance criteria for BFB, then a continuing calibration standard may be injected.

2.8 Documentation

Once the initial calibration is validated, calculate and report the average relative response factor ($\overline{RRF}$) and percent relative standard deviation (%RSD) for all TCL compounds. The Laboratory shall complete and submit a Form V-VOA (Volatile Organic Instrument Performance Check) and Form VI-VOA (Volatile Organic Initial Calibration) for each instrument used to analyze samples under this Protocol. Detailed instructions for completion of Form VI-VOA are found in Exhibit B. The documentation also includes GC/MS data system printout for the analysis of each volatile calibration standard.

TABLE 5 - RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION OF VOLATILE ORGANIC COMPOUNDS

Volatile Compound	Minimum RRF	Maximum %RSD	Maximum %Diff
Chloromethane	0.010	100.	100.
Bromomethane	0.100	30.0	30.0
Vinyl Chloride	0.100	30.0	30.0
Chloroethane	0.010	100.	100.
Methylene chloride	0.010	100.	100.
Acetone	0.010	100.	100.
Carbon disulfide	0.010	100.	100.
1,1-Dichloroethene	0.100	30.0	30.0
1,1-Dichloroethane	0.200	30.0	30.0
1,2-Dichloroethene (total)	0.010	100.	100.
Chloroform	0.200	30.0	30.0
1,2-Dichloroethane	0.100	30.0	30.0
1,2-Dichloroethane-d_4	0.010	100.	100.
2-Butanone	0.010	100.	100.
1,1,1-Trichloroethane	0.100	30.0	30.0
Carbon tetrachloride	0.100	30.0	30.0
Bromodichloromethane	0.200	30.0	30.0
1,2-Dichloropropane	0.010	100.	100.
cis-1,3-Dichloropropene	0.200	30.0	30.0
Trichloroethene	0.300	30.0	30.0
Dibromochloromethane	0.100	30.0	30.0
1,1,2-Trichloroethane	0.100	30.0	30.0
Benzene	0.500	30.0	30.0
trans-1,3-Dichloropropene	0.100	30.0	30.0
Bromoform	0.100	30.0	30.0
2-Hexanone	0.010	100.	100.
4-Methyl-2-pentanone	0.010	100.	100.
Tetrachloroethene	0.200	30.0	30.0
1,1,2,2-Tetrachloroethane	0.500	30.0	30.0
Toluene	0.400	30.0	30.0
Toluene-d_8	0.010	100.	100.
Chlorobenzene	0.500	30.0	30.0
Ethylbenzene	0.100	30.0	30.0
Styrene	0.300	30.0	30.0
Xylenes (total)	0.300	30.0	30.0
Bromofluorobenzene	0.200	30.0	30.0

Section 3. -- GC/MS Continuing Calibration for Target Compounds and System Monitoring Compounds.

Once the GC/MS system has been calibrated, the calibration must be verified each twelve (12) hour time period for each GC/MS system.

3.1 The concentration of the continuing calibration standard for volatile target compounds and system monitoring compounds is 50 µg/L.

3.2 A check of the calibration curve must be performed once every 12 hours (see Paragraph 1. for the definition of the twelve hour time period). Check the relative response factors of those compounds for which RRF values have been established. If these criteria are met, the relative response factors for all compounds are calculated and reported. A percent difference of the daily relative response factor (12 hour) compared to the average relative response factor from the initial curve is calculated. Calculate the percent difference for each compound and compare with the maximum percent difference criteria listed above. For negative percent difference values, the value must be greater than or equal to -25.0%, but less than 0%. As with the initial calibration, up to two volatile compounds in Table 5 may fail to meet the minimum RRF or maximum %D criteria, but the RRFs of those two compounds must be greater than or equal to 0.010, and the percent differences must be less than or equal to 40.0% for the continuing calibration to be acceptable.

3.3 The continuing calibration of the GC/MS system is evaluated on the basis of the magnitude of the relative response factors and the percent difference between the average RRF of each compound from the initial calibration and the RRF of that compound in the continuing calibration standard. The minimum RRF of each compound in the continuing calibration and the percent difference must meet the criteria given in Table 4. Allowance is made for any two volatile compounds that fail to meet these criteria. The minimum RRFs of those two compounds must be greater than or equal to 0.010, and the percent difference must be less than or equal to 40.0% for the continuing calibration to be acceptable.

3.4 The documentation includes Form VII VOA, a GC/MS data system printout for the analysis of the volatile calibration standard.

Section 4. -- Internal Standard Responses and Retention Times

The response of each of the internal standards in all calibration standards, samples, and blanks is crucial to the provision of reliable analytical results, because the quantitative determination of volatile compounds by these procedures is based on the use of internal standards added immediately prior to analysis.

4.1 The following compounds are used as internal standards, Chlorobenzene-d_5, and 1,4-Difluorobenzene in methanol at the concentration of 12.5 µg/mL for each internal standard. Addition of 10 µL of this spiking solution into 25.0 mL of sample or calibration standard results in a concentration of 5 µg/L.

4.2 The retention time and the extracted ion current profile (EICP) of each internal standard must be monitored for all analyses.

4.3 The area response of each internal standard from the EICP and the retention time of the internal standard must be evaluated for stability during or immediately after data acquisition. If the retention time for any internal standard changes by more than ±0.50 minutes (30 seconds) of its retention time from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. For samples analyzed during the same 12-hour period as the initial calibration standards, compare the internal standard responses and retention times against the 5 µg/L calibration standard. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

4.4 The documentation includes Form VIII VOA, and the GC/MS data system printout for the analysis of each sample, blank, matrix spike, matrix spike duplicate, matrix spike blank, and standard.

Section 5 -- Method Blank Analysis

A method blank is a volume of a clean reference matrix (deionized, distilled laboratory water for water samples, or a purified solid matrix for soil/sediment samples) that is carried through the entire analytical scheme. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of the blank is to determine the levels of contamination associated with the processing and analysis of samples.

5.1 For volatile analysis, a method blank must be analyzed once every twelve (12) hours, on each GC/MS system used for volatile analysis (see Paragraph 1. for the definition of the twelve hour time period).

5.1.1 A low concentration volatile method blank consists of a 5 mL volume of reagent water spiked with the system monitoring compounds and internal standards, and carried through the analytical procedure.

5.1.1.1 An acceptable low concentration volatile method blank must contain less than or equal to five times (5x) the Contract Required Quantitation Limit (CRQL, see Exhibit C) of Methylene chloride, Acetone, and 2-Butanone, less than or equal to the CRQL of any other volatile target compound, and no TICs at greater than 10% of the nearest internal standard.

5.1.1.2 All volatile analyses associated with a blank that does not meet the requirements above, (i.e., a contaminated blank) must be repurged, reanalyzed, and reported at no additional cost to the NYSDEC.

5.1.1.3 The volatile method blank must be analyzed after the calibration standards, to ensure that there is no carryover of material from the standards into samples.

5.1.2 The Laboratory must demonstrate that there is no carryover from a contaminated sample before data from subsequent analyses may be submitted. After a sample that contains a target compound at a level exceeding the initial calibration range, the Laboratory must either:

5.1.2.1 Analyze a method blank immediately after the contaminated sample. If an autosampler is used, a method blank must also be analyzed using the same purge inlet that was used for the contaminated sample. The method blanks must meet the technical acceptance criteria for blank analysis, or

5.1.2.2 Monitor the sample analyzed immediately after the contaminated sample for all compounds that were in the contaminated sample and that exceeded the limits above. The maximum contamination criteria are as follows: the sample must not contain a concentration above the CRQL for the target compounds that exceeded the limits in the contaminated sample. If an autosampler is used, the next sample analyzed using the same purge inlet that was used for the contaminated sample also must meet the maximum contamination criteria.

5.2 If a laboratory method blank exceeds these criteria, the Laboratory must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) MUST be reextracted/repurged and reanalyzed at no additional cost to the NYSDEC. The Laboratory Manager, or his designee, must address problems and solutions in the SDG Narrative (Exhibit B).

5.4 The documentation includes Form I VOA for the blank analysis, Form IV VOA, associating the samples and the blank, and a GC/MS data system printout for the analysis of the method blank.

Section 6 -- System Monitoring Compound Recoveries

The recoveries of the three system monitoring compounds are calculated from the analysis of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank. The purpose of the system monitoring compounds is to evaluate the performance of the entire purge and trap-gas chromatograph-mass spectrometer system. Poor purging efficiency, leaks, and cold spots in transfer lines are only a few of the potential causes of poor recovery of these compounds.

6.1 The system monitoring compounds are added to each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank prior to purging, at the following concentrations; Toluene-d_8, p-Bromofluorobenzene, and 1,2-Dichloroethane-d_4 are prepared in Methanol at a concentration of 5.0 µg/mL. Addition of 10.0 µL of this spiking solution into 5.0 mL of sample, results in a concentration of 50 µg/L.

6.2 Calculate the recovery of each system monitoring compound in all samples, blanks, matrix spikes, matrix spike duplicates and matrix spike blanks. Determine if recovery is within limits (see Table 6), and report on appropriate form.

6.2.1 Calculate the concentrations of the system monitoring compounds using the same equation as used for target compounds. Calculate the recovery of each system monitoring compound as follows:

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

6.2.2 If recovery of any one system monitoring compound is not within Protocol limits, the following are required:

- Check to be sure there are no errors in calculations, formulation of the system monitoring compound spiking solutions, and internal standards. Also, check instrument performance.

- Reanalyze the sample if none of the above steps reveal a problem.

- If an undiluted analysis with acceptable monitoring compound recoveries is being submitted, do not reanalyze diluted samples if the system monitoring compound recoveries are outside the limits.

- Never reanalyze the matrix spike, matrix spike duplicate, or matrix spike blank (MS/MSD/MSB), even if the system monitoring compound recoveries are outside the limits.

- If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications, it should be reanalyzed only if the MS/MSD system monitoring compound recoveries are within the limits. If the sample and associated MS/MSD show the same pattern (i.e., outside the limits), then the sample does not require reanalysis and a reanalysis must not be submitted. Document in the narrative the similarity in recoveries of the system monitoring compounds in the sample and associated MS/MSD.

6.2.3 If the reanalysis of the sample solves the problem, then the problem was within the Laboratory's control. Therefore, only submit data from the analysis with system monitoring compound recoveries within the Protocol limits. This shall be considered the initial analysis, it shall be reported as such on all data deliverables, and it must meet holding time requirements specified in Exhibit I.

6.2.4 If the reanalysis of the sample does not solve the problem, (i.e., system monitoring compound recoveries are outside the Protocol limits for both analyses), then submit the data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes specified in Exhibit B.

6.2.5 If the sample with system monitoring compound recoveries outside the Protocol limits is the sample used for the matrix spike and matrix spike duplicate, and the system monitoring compound recoveries of the matrix spike and

matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike, and matrix spike duplicate do not require reanalysis. Document in the narrative the similarity in system monitoring compound recoveries.

6.2.6 Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, if the volatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

6.2.7 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the SDG Narrative.

6.2.8 If the recovery of any one system monitoring compound in a method blank is outside the limits, then the method and all associated samples must be reanalyzed at no additional cost to the NYSDEC.

6.3 The documentation includes Form II VOA, and a GC/MS data system printout for the analysis of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank.

TABLE 6
SYSTEM MONITORING COMPOUND RECOVERY LIMITS

Compound	%Recovery
Toluene-d_8	88 - 110
Bromofluorobenzene	86 - 115
1,2-Dichloroethane-d_4	76 - 114

Section 7 -- Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Analysis (MS/MSD/MSB)

In order to evaluate the effects of the sample matrix upon the methods used for volatile analyses, the NYSDEC has prescribed a mixture of volatile target compounds to be spiked into two aliquots of sample, and one aliquot of reagent water, and analyzed in accordance with the appropriate method.

7.1 A matrix spike and matrix spike duplicate must be performed on those samples so designated by the Contract Lab Sample Information Sheet. If no sample is so designated the Laboratory shall select a sample for spiking for each group of samples of a similar matrix, once:

- each SDG of field samples received, OR
- each 20 field samples in a SDG, OR
- each group of samples of a similar concentration level (soils only), OR
- each 7 calendar day period during which samples in an SDG were received (said period beginning with the receipt of the first sample in that SDG),

whichever is most frequent

UNLESS DIRECTED OTHERWISE BY BWAR OR THE PROJECT OFFICER.

A matrix spike blank must be prepared and analyzed each time MS/MSD samples are prepared to substantiate that any deviations in spike recovery are due to matrix effects and not improper spiking solutions.

7.2 Use the compounds listed in Table 7 to prepare matrix spiking solutions according to procedures described below. The analytical protocols for low/ concentration volatile organics in Exhibit D require that a uniform amount of matrix spiking solution be added to the sample aliquots and to a matrix spike blank prior to extraction/analysis. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate sample.

7.2.1 Volatile Matrix Standard Spiking Solution

7.2.1.1 Prepare a spiking solution in methanol that contains the following compounds at a concentration of 5.0 µg/mL: 1,1 Dichloroethene, Trichloroethene, Chlorobenzene, Toluene, and Benzene. Prepare fresh spiking solution weekly, or sooner, if the solution has degraded or evaporated.

7.2.1.2 Matrix spikes also serve as duplicates; therefore, add an aliquot of this solution to each of two portions from one sample chosen for spiking.

Table 7

Volatiles	
Chlorobenzene	1,1-Dichloroethene
Toluene	Trichloroethene
Benzene	

7.2.2 Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

7.3 Individual component recoveries for the matrix spike sample and blank are calculated using Equation 7.1.

Equation 7.1

$$\text{Matrix Spike Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike Sample Results

SR = Sample Result

SA = Spike Added from spiking mix

7.4 Relative Percent Difference (RPD)

The Laboratory to calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using Equation 7.2.

Equation 7.2

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

Where:

RPD = Relative Percent Difference

D_1 = First Sample Value

D_2 = Second Sample Value (duplicate)

7.5 Documentation

The matrix spike (MS) results (concentrations) for all volatile TCL compounds shall be reported on Form I-VOA (Volatile Organic Analysis Data Sheet) and the matrix spike percent recoveries shall be summarized on Form III-VOA (MS/MSD Recovery).

The results for all volatile TCL compounds in the matrix spike duplicate (MSD) analysis shall be reported on Form I-VOA (Volatile Organic Analysis Data Sheet) and the percent recovery and the relative percent difference shall be summarized on Form III-VOA (MS/MSD Recovery). See Exhibit B for detailed instructions on the completion of Form III-VOA.

The results for all volatile TCL compounds in the matrix spike blank analysis shall be reported on Form I-VOA (Volatile Organic Analysis Data Sheet) and the matrix spike percent recoveries shall be summarized on Form III-VOA (MS/MSD Recovery).

TABLE 8
MATRIX SPIKE RECOVERY AND
RELATIVE PERCENT DIFFERENCE LIMITS*

Compound	%Recovery	RPD
1,1-Dichloroethane	61-145	14
Trichloroethene	71-120	14
Benzene	76-127	11
Toluene	76-125	13
Chlorobenzene	75-130	13

TABLE 9
MATRIX SPIKE BLANK RECOVERY LIMITS*

Compound	%Recovery
1,1-Dichloroethane	61 - 145
Trichloroethene	71 - 120
Benzene	76 - 127
Toluene	76 - 125
Chlorobenzene	75 - 130

* These limits are for advisory purposes only. They are not to be used to determine if a sample should be reanalyzed. When sufficient multi-lab data are available, standard limits will be calculated.

7.6 The quality control limits for recovery and relative percent difference are given in Table 8. These limits are only advisory at this time, and no further action is required when the limits are exceeded.

7.7 The documentation includes Form I VOA for the MS, MSD and MSB analyses, Form III VOA, and a GC/MS printout for each analysis.

Section 8. -- Dilution of Samples, Matrix Spikes, and Matrix Spike Duplicates

If the on-column concentration of any sample exceeds the initial calibration range, that sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions are given below.

8.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.2 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

8.3 Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, if the volatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

8.4 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the SDG Narrative.

8.5 For total Xylenes, where three isomers are quantified as two peaks, the calibration of each peak, should be considered separately, i.e., a diluted analysis is not required for total Xylenes unless the concentration of either peak separately exceeds 50 µg/L.

Part X -- Requirements For Low Concentration Semivolatile Organics In Water By GC/MS (Methods CLP Low Organics)

Parts II and III of this Exhibit outline the requirements for the quality assurance program that each laboratory must establish under this Protocol. This Part outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with the determination of semi-volatile organic compounds in water and soil/sediment samples. This section is not intended as a comprehensive quality control document, but rather as a guide to the specific QC operations that must be considered for semivolatile analyses. At a minimum, the Laboratory is expected to address these operations in preparing the quality assurance plan and QA/QC Standard Operating Procedures discussed in Section II.

These QC operations are as follows:

- GC/MS Mass Calibration and Abundance Pattern
- GC/MS Initial and Continuing Calibration
- Stability of Internal Standard Response and Retention Times
- Method Blank Analysis
- Surrogate Recoveries
- Matrix Spike, Matrix Spike Duplicate, and Matrix Spike Blank Analysis
- Dilution of Samples, Matrix Spikes, and Matrix Spike Duplicates

Section 1 -- GC/MS Mass Calibration and Ion Abundance Patterns

Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that a given GC/MS system meets the instrument performance criteria specified below. The purpose of this instrument performance check is to assure correct mass calibration, mass resolution, and mass transmission. This is accomplished through the analysis of Decafluorotriphenylphosphine (DFTPP).

1.1 Each GC/MS system used for the analysis of semivolatile or pesticide compounds must be hardware tuned to meet the abundance criteria listed in Table 1. for a 50 ng injection of decafluorotriphenylphosphine (DFTPP). DFTPP may be analyzed separately or as part of the calibration standard. The criteria must be demonstrated daily or for each twelve (12) hour period, whichever is more frequent, before samples can be analyzed. DFTPP must be injected to meet this criteria. If required, background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the protocol specifications are unacceptable.

***NOTE**: All instrument conditions must be identical to those used in sample analysis, except that a different temperature program may be used.*

1.2 The instrument performance check solution must be analyzed once at the beginning of each 12-hour period during which samples or standards are analyzed.

The twelve (12) hour time period for a GC/MS system instrument performance check and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after twelve (12) hours has elapsed according to the system clock.

1.3 The key ions produced during the analysis of DFTPP and their respective ion abundance criteria are given in Table 1.

TABLE 1
DFTPP KEY IONS AND ION ABUNDANCE CRITERIA FOR QUADRAPOLE MASS SPECTROMETERS

Mass	Ion Abundance Criteria
51	30.0 - 60.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	40.0 - 60.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 1.00 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110.0 percent of mass 198
443	17.0 - 23.0 percent of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent that of m/z 198.

Whenever the Laboratory takes corrective action which may change or affect the instrument performance criteria for DFTPP (e.g., ion source cleaning or repair, etc.), the mass calibration must be verified irrespective of the 12-hour calibration requirements.

1.4 Documentation

The Laboratory shall provide documentation of the calibration in the form of a bar graph spectrum and as a mass listing.

1.4.1 The Laboratory shall complete a Form V-CLP-SV (Semivolatile Organic Instrument Performance Check) each time an Instrument Performance Check is performed. In addition, all samples, standards, blanks, matrix spikes, and matrix spike duplicates analyzed during a particular 12-hour sequence must be summarized in chronological order on the bottom of the appropriate Form V-CLP-SV. Detailed instructions for the completion of Form V-SVA are found in Exhibit B, Section III.

Section 2 -- GC/MS Initial Calibration for Target Compounds and Surrogates

Prior to the analysis of samples and required blanks and after instrument performance criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations, analyzed consecutively under the same DFTPP Instrument Performance Check, to determine the linearity of response utilizing Superfund-TCL compound standards.

2.1 Five initial calibration standard solutions are required for all target compounds and surrogates. Standard concentrations of 5, 10, 20, 50, and 80 µg/mL, are required for all the surrogates and all but nine of the target compounds. Nine compounds: 2,4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, Pentachlorophenol, and 2,4,6-Tribromophenol (surrogate), require calibration at 20, 50, 80, 100 and 120 µg/mL.

2.2 The standards are to be analyzed according to the procedures given below.

2.2.1 Prior to the analysis of samples and required blanks, and after the instrument performance check solution criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the semivolatile target compounds.

2.2.2 The internal standards are added to all calibration standards and all sample extracts (including blanks, matrix spikes, matrix spike duplicates, and matrix spike blanks) just prior to analysis by GC/MS. A 10 µL aliquot of the internal standard solution should be added to a 1 mL aliquot of calibration standards. The internal standards specified below should permit most of the semivolatile target compounds to have relative retention times of 0.80 to 1.20, using the assignments of internal standards to target compounds given in Table 2.

2.2.3 Internal standards - 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, Perylene-d_{12}.

An internal standard solution can be prepared by dissolving 100 mg of each compound in 50 mL of methylene chloride. It may be necessary to use 5 to 10 percent benzene or toluene in this solution and a few minutes of ultrasonic mixing in order to dissolve all the constituents. The resulting solution will contain each standard at a concentration of 2000 µg/mL. A 10 µL portion of this solution should be added to each 1 mL of sample extract. This will result in 20 µg/mL of each internal standard in the 1 µL volume of extract injected into the GC/MS.

2.2.4 The quantitation ions for each internal standard are given in Table 3. Use the primary ion listed in Table 3 for quantitation, unless interferences are present. If interferences prevent the use of the primary ion for a given internal standard, use the secondary ion(s) listed in Table 3.

2.2.5 Analyze 1 µL of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. A 1 µL injection is required. Calculate relative response factors (RRF) for each compound using Equation 1.

Equation 1.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured (see Table 4).

A_{is} = Area of the characteristic ion for the specific internal standard (see Table 3).

C_{is} = Concentration of the internal standard (µg/mL).

C_x = Concentration of the compound to be measured (µg/mL).

TABLE 2 - SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SURROGATES ASSIGNED FOR QUANTITATION IN LOW CONCENTRATION METHODS

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene
bis(2-Chloroethyl) ether	Isophorone	2 ,4, 6-Trichloro-phenol
2-Chlorophenol	2-Nltrophenol	2,4,5-Trichloro-phenol
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Chloronaphthalene
1,4-Dichlorobenzene	bis(2-Chloro-ethoxy)methane	2-Nitroaniline
1,2-Dichlorobenzene	2,4-Dichloro-phenol	Dimethyl phthalate
2-Methylphenol	1,2,4-Trichloro benzene	Acenaphthylene
2,2'-oxybis-(1-Chloropropane)	Naphthalene	3-Nitroaniline
4-Methylphenol	4-Chloroaniline	Acenaphthene
N-Nitroso-di-n-propylamine	Hexachloro-butadiene	2,4-Dinitrophenol
Hexachloroethane	4-Chloro-3-methylphenol	4-Nitrophenol
2-Fluorophenol (surr)	2-Methylnaphth-alene	Dibenzofuran
Phenol-d_5 (surr)	Nitrobenzene-d_5 (surr)	2,4-Dinitrotoluene
2-Chlorobenzene-d_4 (surr)		2,6-Dinitrotoluene
1, 2-Dichlorobenzene-d_4 (surr)		Diethyl phthalate
		4-Chlorophenyl phenyl ether
		Fluorene
		4-Nitroaniline
		2-Fluorobiphenyl (surr)
		2,4,6-Tribromo-phenol (surr)

surr = surrogate compound

TABLE 2 - SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SURROGATES ASSIGNED FOR QUANTITATION IN LOW CONCENTRATION METHODS (continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4, 6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl-phthalate
N-Nitrosodi-phenylamlne	Butylbenzyl phthalate	Benzo(b)fluor-anthene
4-Bromophenyl phenyl ether	3,3'-Dichloro-benzidlne	Benzo(k)fluor-anthene
Hexachloro-benzene	Benzo(a)-anthracene	Benzo(a)pyrene
Pentachloro-phenol	bis(2-Ethyl-hexyl)phthalate	Indeno(1,2,3-cd)-pyrene
Phenanthrene	Chrysene	Dibenz(a,h)-anthracene
Carbazole	Terphenyl-d_{14} (surr)	Benzo(g,h,i)-perylene
Anthracene		
Di-n-butyl-phthalate		
Fluoranthene		

surr = surrogate compound

TABLE 3 - CHARACTERISTIC IONS FOR INTERNAL STANDARDS FOR SEMIVOLATILE COMPOUNDS

INTERNAL STANDARDS	Primary Ion	Secondary Ions
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenapthene-d_{10}	164	162,160
Phenanthrene-d_{10}	188	94,80
Chrysene-d_{12}	240	120,236
Perylene-d_{12}	264	260,265

TABLE 4 - CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS AND SURROGATES

Parameter	Primary Ion	Secondary Ion(s)
Phenol	94	65,66
bis(2-Chloroethyl)ether	93	63,95
2-Chlorophenol	128	64,130
1,3-Dichlorobenzene	146	148,113
1,4-Dichlorobenzene	146	148,113
1,2-Dichlorobenzene	146	148,113
2-Methylphenol	108	107
2,2'-oxybis(1-Chloropropane)	45	77,79
4-Methylphenol	108	107
N-Nitroso-di-propylamine	70	42,101,130
Hexachloroethane	117	201,199
Nitrobenzene	77	123,65
Isophorone	82	95,138
2-Nitrophenol	139	65,109
2,4-Dimethylphenol	107	121,122
bis(2-Chloroethoxy)methane	93	95,123
2,4-Dichlorophenol	162	164,98
1,2,4-Trichlorobenzene	180	182,145
Naphthalene	128	129,127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223,227
4-Chloro-3-methylphenol	107	144,142
2-Methylnaphthalene	142	141
Hexach}orocyclopentadiene	237	235,272
2,4,6-Trichlorophenol	196	198,200
2,4,5-Trichlorophenol	196	198,200
2-Chloronaphthalene	162	164,127
2-Nitroaniline	65	92,138
Dimethyl phthalate	163	194,164
Acenaphehylene	152	151,153
3-Nitroaniline	138	108,92
Acenaphthene	153	152,154
2,4-Dinitrophenol	184	63,154
4-Nitrophenol	109	139,65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63,182
2,6-Dinitrotoluene	165	89,121

(continued)

TABLE 4 - CHARACTERISTIC IONS FOR SEMIVOLATILE TARGET COMPOUNDS AND SURROGATES (continued)

Parameter	Primary Ion	Secondary Ion(s)
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Carbazole	167	166, 139
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzldine	252	254, 126
Benzo(a)anthracene	228	229, 226
bis(2-Ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-Octyl phthalate	149	---
Benzo(b)fluoranehene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
SURROGATES		
Phenol-d_5	99	42, 71
2-FluorophenoL	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-d_5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
2-Chlorophenol-d_4	132	68, 134
1,2-Dichlorobenzene-d_4	152	115, 150

2.3 The average relative response factor ($\overline{RRF}$) must be calculated for all compounds. Calculate the %Relative Standard Deviation (%RSD) of RRF values for the initial calibration using Equation 2:

Equation 2.

$$\%RSD = \frac{\text{Standard Deviation}}{\text{mean}} \times 100$$

Where:

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}{n - 1}}$$

Where:

x_i = each individual value used to calculate the mean

$\overline{x}$ = the mean of n values

n = the total number of values

2.4 Response factor criteria have been established for the calibration of the semivolatile target compounds and semivolatile surrogate compounds.

2.4.1 The response factors of the compounds listed in Table 5 must meet the minimum RRF criteria at each concentration level and maximum RSD criteria for the initial calibration, with allowance made for up to four semivolatile target and surrogate compounds. However, the RRFs for those four compounds must be greater than 0.010, and the %RSD of those four compounds must be less than or equal to 40.0% for the initial calibration to be acceptable.

TABLE 5 - RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION OF SEMIVOLATILE TARGET COMPOUNDS

Semivolatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Diff
Phenol	0.800	20.5	25.0
bis(2-Chloroethyl)ether	0.700	20.5	25.0
2-Chlorophenol	0.800	20.5	25.0
1,3-Dichlorobenzene	0.600	20.5	25.0
1,4-Dfchlorobenzene	0.500	20.5	25.0
1,2-Dichlorobenzene	0.400	20.5	25.0
2-Methylphenol	0.700	20.5	25.0
4-Methylphenol	0.600	20.5	25.0
N-Nitroso-di-propylamine	0.500	20.5	25.0
Hexachloroethane	0.300	20.5	25.0
Nitrobenzene	0.200	20.5	25.0
Isophorone	0.400	20.5	25.0
2-Nitrophenol	0.100	20.5	25.0
2,4-Dimethylphenol	0.200	20.5	25.0
bis(2-Chloroethoxy)methane	0.300	20.5	25.0
2,4-Dichlorophenol	0.200	20.5	25.0
1,2,4-Trichlorobenzene	0.200	20.5	25.0
Naphthalene	0.700	20.5	25.0
4-Chloro-3-methylphenol	0.200	20.5	2S.0
2-Methylnaphthalene	0.400	20.5	25.0
2,4,6-Trichlorophenol	0.200	20.5	25.0
2,4,5-Trlchlorophenol	0.200	20.5	25.0
2-Chloronaphthalene	0.800	20.5	25.0
Acenaphthylene	1.300	20.5	25.0
2,6-Dinitrotoluene	0.200	20.5	25.0
Acenaphthene	0.800	20.5	25.0
Dibenzofuran	0.800	20.5	25.0
2,4-Dinitrotoluene	0.200	20.5	25.0
4-Chlorophenyl-phenylether	0.400	20.5	25.0
Fluorene	0.900	20.5	25.0
4-Bromophenyl-phenylether	0.100	20.5	25.0
Hexachlorobenzene	0.100	20.5	25.0
Pentachlorophenol	0.050	20.5	25.0

(continued)

TABLE 5 - RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION OF SEMIVOLATILE TARGET COMPOUNDS (continued)

Semivolatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Diff
Phenanthrene	0.700	20.5	25.0
Anthracene	0.700	20.5	25.0
Fluoranehene	0.600	20.5	25.0
Pyrene	0.600	20.5	25.0
Benzo(a)anthracene	0.800	20.5	25.0
Chrysene	0.700	20.5	25.0
Benzo(b)fluoranthene	0.700	20.5	25.0
Benzo(k)fluoranthene	0.700	20.5	25.0
Benzo(a)pyrene	0.700	20.5	25.0
Indeno(1,2,3-cd)pyrene	0.500	20.5	25.0
Dibenzo(a,h)anthracene	0.400	20.5	25.0
Benzo(g,h,i)perylene	0.500	20.5	25.0
Nitrobenzene-d_5	0.200	20.5	25.0
2-Fluorobiphenyl	0.700	20.5	25.0
Terphenyl-d_{14}	0.500	20.5	25.0
Phenol-d_5	0.800	20.5	25.0
2-Fluorophenol	0.600	20.5	25.0
2-Chlorophenol-d_4	0.800	20.5	25.0
1,2-Dichlorobenzene-d_4	0.400	20.5	25.0

2.4.2 The following compounds have a Maximum %RSD of 100%, and a Maximum %Difference of 100%; and, these compounds must meet a minimum RRF criterion of 0.010:

2,2'-oxybis(1-Chloropropane)	4-Nitroaniline
4-Chloroaniline	4,6-Dinitro-2-methylphenol
Hexachlorobutadiene	N-Nitrosodiphenylamine
Hexachlorocyclopentatiene	Di-n-butylphthalate
2-Nitroaniline	.Butylbenzylphthalate
Dimethylphthalate	3,3'-Dichlorobenzidine
3-Nitroaniline	bis(2-Ethylhexyl)phthalate
2,4-Dinitrophenol	Di-n-octylphthalate
4-Nitrophenol	2,4,6-Tribromophenol
Diethylphthalate	Carbazole

2.5 The calibration of the GC/MS is evaluated on the basis of the magnitude and stability of the relative response factors of each target compound and surrogate. The minimum RRF of each compound at each concentration level in the initial calibration and the percent relative standard deviation (%RSD) across all five points must meet the criteria given in Table 5. Allowance is made for any four semivolatile compounds that fail to meet these criteria. The minimum RRFs of those four

compounds must be greater than or equal to 0.010, and the %RSD must be less than or equal to 40.0% for the initial calibration to be acceptable.

2.6 The documentation includes Form VI-CLP-SV, a GC/MS data system printout for the analysis of each semivolatile calibration standard.

Section 3. -- GC/MS Continuing Calibration for Target Compounds and Surrogates.

Once the GC/MS system has been calibrated, the calibration must be verified each twelve (12) hour time period for each GC/MS system.

3.1 The level of the continuing calibration standard for semivolatile target compounds and surrogates is 20 ng, except for nine compounds (2,4-Dinitrophenol, 2,4,5-Trichlorophenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, Pentachlorophenol, and 2,4,6-Tribromophenol (surrogate)) which are at 80 ng in a 2 µL injection volume, as described in Paragraph 2.2 above.

3.2 A check of the calibration curve must be performed once every 12 hours (see Paragraph 1.2 for the definition of the twelve-hour time period). Check the relative response-factors of those compounds for which RRF values have been established. If these criteria are met, the relative response factors for all compounds are calculated and reported. A percent difference of the daily relative response factor (12 hour) compared to the average relative response factor from the initial curve is calculated. Calculate the percent difference for each compound using Equation 3. and compare with the maximum percent difference criteria listed above.

Equation 3.

$$\% \text{ Difference} = \frac{\left| \overline{RRF_i} - RRF_c \right|}{\overline{RRF_i}} \times 100$$

Where:

$\overline{RRF_i}$ = average relative response factor from initial calibration.

RRF_c = relative response factor from current calibration check standard.

3.3 The continuing calibration of the GC/MS system is evaluated on the basis of the magnitude of the relative response factors and the percent difference between the average RRF of each compound from the initial calibration and the RRF of that compound in the continuing calibration standard. The minimum RRF of each compound in the continuing calibration and the percent difference must meet the criteria given in Table 5. Allowance is made for any four semivolatile compounds that fail to meet these criteria. The minimum RRFs of those four compounds must be greater than or equal to 0.010, and the %D must be less than or equal to 40.0% for the continuing calibration to be acceptable.

3.4 The documentation includes Form VII-CLP-SV, a GC/MS data system printout for the analysis of the semivolatile calibration standard.

Section 4. -- Internal Standard Responses and Retention Times

The response of each of the internal standards in all calibration standards, samples, and blanks is crucial to the provision of reliable analytical results because the quantitative determination of semivolatile compounds by these procedures is based on the use of internal standards added immediately prior to analysis.

4.1 The specific compounds used as internal standards are given in Paragraph 2.2.3. The amount of each internal standard in the injection volume (2 µL) of the sample extract analyzed by GC/MS must be 40 ng (20 µg/mL).

4.2 The retention time and the extracted ion current profile (EICP) of each internal standard must be monitored for all analyses.

4.3 TCL semivolatile organic components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte (see Tables 1 and 2). The EICP area of characteristic ions of analytes listed in Table 4 are used for quantitation. In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify such edits or manual procedures by initializing and dating the changes made to the report.

Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 0.50 minutes (30 seconds) from the latest daily (12 hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. For samples analyzed during the same 12-hour time period as the initial calibration standards, compare the internal standard responses and retention times to those of the 20 ng or 80 ng (as appropriate) calibration standard. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike blank, matrix spike, and matrix spike duplicate. The criteria are described in detail in the instructions for Form VIII, Internal Standard Area Summary. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. If the analysis of a subsequent sample or standard indicates that the system is functioning properly, then corrections may not be required. The samples or standards with EICP areas outside the limits must be re-analyzed, and treated according to 4.3.1 and 4.3.2 below. If corrections are made, then the Laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accomplished by the analysis of a standard or sample that <u>does</u> meet the EICP criteria. After corrections are made, the re-analysis of samples analyzed while the system was malfunctioning is required.

4.3.1 If after re-analysis, the EICP areas for all internal standards are inside the Protocol limits (-50% to +100%), then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, <u>only submit</u> data from the analysis with EICP's within the Protocol limits. This is

considered the initial analysis, it must be reported as such on all data deliverables, and it must meet holding time requirements specified in Exhibit I.

4.3.2 If the re-analysis of the sample does not solve the problem, i.e., the EICP areas are outside the Protocol limits for both analyses, then submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables, using the sample suffixes specified in Exhibit B. Document in the SDG Narrative all inspection and corrective actions taken.

4.3.3 Do not re-analyze MS/MSD samples that do not meet the EICP area limits.

4.4 The documentation includes Form VIII SV, and the GC/MS data system printout for the analysis of each sample, blank, matrix spike, matrix spike duplicate, matrix spike blank and standard.

Section 5 -- Method Blank Analysis

A method blank is a volume of a clean reference matrix (deionized, distilled laboratory water for water samples, or a purified solid matrix (sodium sulfate) for soil/sediment samples), that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

5.1 Method blank analysis must be performed once for the following, on each GC/MS system used to analyze samples, whichever is most frequent:

- Each SDG, OR
- Each 7 calendar day period during which samples in an SDG are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), OR
- Each 20 samples in an SDG, including matrix spikes and re-analyses, that are of similar matrix.

5.2 For the purposes of this Protocol, an acceptable method blank must meet the criteria in paragraphs 5.2.1. and 5.2.2 below.

5.2.1 A method blank for semivolatile analysis must contain less than or equal to five times (5x) the Contract Required Quantitation Limit (CRQL, see Exhibit C) of the phthalate esters listed in Ex. C.

5.2.2 For all other target compounds, the method blank must contain less than or equal to the Contract Required Quantitation Limit (CRQL, see Exhibit C) of any single target compound.

5.3 If a method blank exceeds the limits for contamination above, the Laboratory must consider the analytical system out of control. The source of the

contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) MUST be re-extracted and re-analyzed at no additional cost to the NYSDEC. The Laboratory Manager, or his designee, must address problems and solutions in the SDG Narrative (Exhibit B).

5.4 The documentation includes Form I-CLP-SV for the blank analysis, Form IV-CLP-SV, associating the samples and the blank, and a GC/MS data system printout for the analysis of the method blank.

Section 6 -- Surrogate Recoveries

The recoveries of the eight surrogates are calculated from the analysis of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank. The purpose of the surrogates is to evaluate the preparation and analysis of samples.

6.1 The surrogates are added to each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank prior to extraction. The compounds specified for this purpose are Phenol-d_5; 2,4,6-Tribromophenol; 2-Fluorophenol; Nitrobenzene-d_5; Terphenyl-d_{14}; 2-Fluorobiphenyl; 2-Chlorophenol-d_4; and 1,2-Dichlorobenzene-d_4. Additional surrogates may be added at the Laboratory's discretion.

6.2 Prepare a surrogate standard spiking solution in methanol that contains the acid compound, 2,4,6-Tribromophenol, at 120 µg/mL concentration. The other acid compounds: Phenol-d_6 and 2-Fluorophenol and the base/neutral compounds: Nitrobenzene-d_5, Terphenyl-d_{14}, and 2-Fluorobiphenyl are at a concentration of 40 µg/mL. Store the spiking solutions at 4°C (±2°C) in Teflon®-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after twelve months, or sooner if comparison with quality control check samples indicate a problem.

6.3 Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits (see Table 6) and report on appropriate form.

6.3.1 Calculate the concentrations of the surrogate compounds using the same equations as used for the target compounds. Calculate the recovery of each surrogate as follows:

Equation 4.

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

6.3.2 Determine if the sample surrogate recovery meets specifications as follows:

- The six semivolatile surrogates can be divided into two groups: base/neutral compounds (Nitrobenzene-d_5, 2-Fluorobiphenyl, and Terphenyl-d_{14}) and acid compounds (Phenol-d_5, 2-Fluorophenol, and 2,4,6-Tribromophenol).

- If a single surrogate recovery from any group is not within the Protocol windows, the sample does not require reanalysis or re-extraction.

- If a single surrogate recovery from the base/neutral group and a single surrogate recovery from the acid group are not within the Protocol windows, the sample does not require reanalysis or re-extraction.

TABLE 6 - SURROGATE RECOVERY LIMITS

Compound	%Recovery
Nitrobenzene-d_5	40 - 112
2-Fluorobiphenyl	42 - 110
Terphenyl-d_{14}	24 - 140
Phenol-d_5	17 - 113
2-Fluorophenol	26 - 110
2,4,6-Tribromophenol	18 - 126

6.3.3 If the sample surrogate recovery does not meet specifications (i.e., if two base/neutral or two acid surrogates are out of limits or if recovery of any one base/neutral or acid surrogate is below 10%), the following are required:

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

- Reanalyze the sample if none of the above reveal a problem.

- If surrogate recoveries in a blank do not meet specifications, the blank may be reanalyzed alone.

- Do not reanalyze dilutions if surrogate recoveries are outside the limits.

- Never reanalyze the matrix spike or matrix spike duplicate (MS/MSD), even if surrogate recoveries are outside the limits.

- If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications, it should be reanalyzed only if the MS/MSD surrogate recoveries are within the limits. If the sample and associated MS/MSD show the same pattern (i.e., outside the limits), then the sample does not require re-analysis and a re-analysis must not be submitted.

- Document in the narrative the similarity in surrogate recoveries.

6.3.4 If the reanalysis of the sample solves the problem, then the problem was within the Laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the Protocol windows. This shall be

considered the initial analysis, it shall be reported as such on all data deliverables, and it must meet holding time requirements specified in Exhibit I.

6.3.5 If none of the steps in 6.3.3 or 6.3.4 solve the problem, then reextract and reanalyze the sample. If the reextraction and reanalysis of the sample solves the problem, then the problem was within the Laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the Protocol windows. This shall be considered the initial analysis, it shall be reported as such on all data deliverables, and it must meet holding time requirements specified in Exhibit I.

- If surrogate recoveries in a blank do not meet specifications even after reanalysis, all of the samples associated with that blank must be re-extracted along with the blank. The blank is intended to detect contamination in samples processed at the same time.

- Do not re-extract diluted samples if surrogate recoveries are outside the limits.

- Never re-extract the matrix spike or matrix spike duplicate (MS/MSD), even if surrogate recoveries are outside the limits.

- If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications after reanalysis, it should be reextracted only if the reanalysis surrogate recoveries are not within the limits and MS/MSD surrogate recoveries are within the limits. If the sample and associated MS/MSD show the same pattern (i.e., outside the limits), then the sample does not require reanalysis and a reanalysis must not be submitted.

- Document in the narrative the similarity in surrogate recoveries.

6.3.6 If the reextraction and reanalysis of the sample does not solve the problem, (i.e., the surrogate recoveries are outside the Protocol limits for both analyses), then submit the surrogate spike recovery data and the sample analysis data from analysis of both sample extracts. Distinguish between the initial analysis and the analysis of the re-extracted sample on all data deliverables, using the sample suffixes specified in Exhibit B.

6.4 The documentation includes Form II SV, and a GC/MS data system printout for the analysis of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank.

Section 7 -- Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Analysis (MS/MSD/MSB)

In order to evaluate the matrix effect of the sample upon the analytical methodology, the NYSDEC has prescribed a mixture of semivolatile target compounds to be spiked into two aliquots of a sample, and one aliquot of reagent water, and analyzed in accordance with the appropriate method.

7.1 A matrix spike, matrix spike duplicate, and matrix spike blank must be performed for each group of samples of a similar matrix, for the following, whichever is most frequent, unless directed differently by the Bureau of Program Services and Research or the Project Officer.

- Each SDG of field samples received, OR
- Each 20 field samples in a Case, OR
- Each 7 calendar day period during which field samples in a Case were received (said period beginning with the receipt of the first sample in that Sample Delivery Group).

Calculate the recovery of each matrix spike compound in the matrix spike, matrix spike duplicate, and matrix spike blank and report on appropriate form.

7.1.1 Calculate the concentrations of the matrix spike compounds using the same equations as used for target compounds. Calculate the recovery of each matrix spike compound using Equation 5.

Equation 5.

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike sample result

SR = Sample result

SA = Spike added

7.1.2 Calculate the relative percent difference of the recoveries of each compound in the matrix spike and matrix spike duplicate using Equation 6.

Equation 6.

$$RPD = \frac{|MSR - MSDR|}{(1/2)(MSR+MSDR)} \times 100$$

Where:

RPD = Relative Percent Difference

MSR = Matrix Spike Recovery

MSDR = Matrix Spike Duplicate Recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

7.1.3 The limits for matrix spike blank recovery are given in Table 7. These limits must be met. Failure to meet these limits will require re-extraction and reanalysis of the matrix spike, matrix spike duplicate and the matrix spike blank.

TABLE 7 - MATRIX SPIKE BLANK RECOVERY LIMITS

Compound	%Recovery
Phenol	12 - 110
2-Chlorophenol	27 - 123
1,4-Dichlorobenzene	36 - 97
N-Nitroso-di-n-propylamine	41 - 116
1,2,4-Trichlorobenzene	39 - 98
4-Chloro-3-methylphenol	23 - 97
Acenaphthene	46 - 118
4-Nitrophenol	10 - 80
2,4-Dinitrotoluene	24 - 96
Pentachlorophenol	9 - 103
Pyrene	26 - 127

7.1.4 The limits for matrix spike compound recovery and RPD are given in Table 8. As these limits are only advisory, no further action by the Laboratory is required, however, frequent failures to meet the limits for recovery or RPD warrant investigation by the Laboratory, and may result in questions from the NYSDEC.

TABLE 8 - MATRIX SPIKE RECOVERY AND
RELATIVE PERCENT DIFFERENCE LIMITS

Compound	%Recovery	RPD
Phenol	12-110	42
2-Chlorophenol	27-123	40
1,4-Dichlorobenzene	36- 97	28
N-Nitroso-di-n-propylamine	41-116	38
1,2,4-Trichlorobenzene	39- 98	28
4-Chloro-3-methylphenol	23- 97	42
Acenaphthene	46-118	31
4-Nitrophenol	10- 80	50
2,4-Dinitrotoluene	24- 96	38
Pentachlorophenol	9-103	50
Pyrene	26-127	31

7.2 The documentation includes Form I SV for the MS, MSD, and MSB analyses, Form III SV, and a GC/MS printout for each analysis.

Section 8. -- Dilution Of Samples, Matrix Spikes, And Matrix Spike Duplicates

If the on-column concentration of any compound in any sample exceeds the initial calibration range, that sample extract must be diluted, the internal standard concentration readjusted, and the sample extract reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

8.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

8.2 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

8.3 Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, if the semivolatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

8.4 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the SDG Narrative.

Part XI -- Requirements For Low Concentration Pesticides And Aroclors In Water By GC/ECD

Parts II and III of this Exhibit outline the requirements for the quality assurance program that each laboratory must establish under this Protocol. This Part outlines the minimum quality control (QC) operations necessary to satisfy the analytical requirements associated with all Exhibit D determinations of pesticide/Aroclor target compounds in water and soil/sediment samples. This section is not intended as a comprehensive quality control document, but rather as a guide to the specific QC operations that must be considered for pesticide/Aroclor analyses. At a minimum, the Laboratory is expected to address these operations in preparing the quality assurance plan and QA/QC Standard Operating Procedures discussed in Part II.

These QC operations include the following:

- GC Column Resolution
- GC/EC Initial and Continuing Calibration
- Determination of Retention times and Retention Time Windows
- Analytical Sequence
- Blank analyses
- Matrix Spike, Matrix Spike Duplicate, and Matrix Spike Blank Analysis
- Dilution of Samples, Matrix Spikes, and Matrix Spike Duplicates

Not discussed in this section are the requirements for quality assurance of the data reporting aspects of pesticide/Aroclor analyses which are described in general terms in Section II and III of this exhibit.

Section 1. -- GC Column Resolution

Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that a given GC column meets the analyte resolution criteria. The purpose of this resolution check is to demonstrate that at the time of the initial calibration, the GC column is capable of chromatographically resolving the target compounds. This is accomplished through the analysis of the Resolution Check Mixture, which contains the nine target compounds that are most difficult to resolve.

1.1 The Resolution Check Mixture must be analyzed at the beginning of every initial calibration sequence, on each GC column and instrument used for analysis. Prepare the mixture of pesticides in hexane or iso-octane at the concentrations listed below. The mixture must be prepared every six months, or sooner if the solution has degraded or concentrated.

Resolution Check Mixture

gamma-Chlordane	10.0 ng/mL	Endrin ketone	20.0 ng/mL
Endosulfan I	10.0 ng/mL	Methoxychlor	100.0 ng/mL
p,p'-DDE	20.0 ng/mL	Tetrachloro-m-xylene	20.0 ng/mL
Dieldrin	20.0 ng/mL	Decachlorobiphenyl	20.0 ng/mL
Endosulfan sulfate	20.0 ng/mL		

1.2 The resolution criterion is that the depth of the valley between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0% of the height of the shorter peak. The poorest resolution on the DB-608 column probably will be between DDE and Dieldrin, between Methoxychlor and Endrin ketone and between Endosulfan I and gamma-Chlordane. On the DB-1701 column, resolution difficulties most frequently occur between Endosulfan I and gamma-Chlordane, and between Methoxychlor and Endosulfan sulfate.

1.3 Additional resolution criteria apply to the target compounds in the standards used for initial calibration and calibration verification.

1.3.1 All peaks in both of the Performance Evaluation Mixtures must be 100 percent resolved on both columns.

1.3.2 The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.

1.4 The documentation includes Form VI PEST-4, chromatograms and data system printouts for the analysis of the Resolution Check Mixture on each GC column and instrument used for analysis.

Section 2. -- GC/EC Initial Calibration For Target Compounds And Surrogates.

Prior to the analysis of samples and required blanks, the GC/EC system must be initially calibrated at a minimum of three concentrations to determine the linearity of response utilizing single component target compound and surrogate standards. Multicomponent target compounds are calibrated at a single point.

2.1 Individual Standard Mixtures A and B - the single component pesticide standards must be prepared in hexane or iso-octane at three concentrations for each analyte, including the surrogates. Two separate calibration mixtures, A and B, (listed below) are used to ensure that each peak is adequately resolved. The low point concentration corresponds to the CRQL for each analyte. The midpoint concentration must be 4 times the low point concentration. The high point concentration must be at least 16 times that of the low point, but a higher concentration may be chosen by the Laboratory. The high point concentration defines the upper end of the concentration range for which the concentration is valid. The solution must be prepared every six months, or sooner if the solution has degraded or concentrated.

Individual Standard Mixture A	Low Point Concentration
alpha-BHC	5.0 ng/mL
Heptachlor	5.0 ng/mL
gamma-BHC	5.0 ng/mL
Endosulfan I	5.0 ng/mL
Dieldrin	10.0 ng/mL
Endrin	10.0 ng/mL
p,p'-DDD	10.0 ng/mL
p,p'-DDT	10.0 ng/mL
Methoxychlor	50.0 ng/mL
Tetrachloro-m-xylene	5.0 ng/mL
Decachlorobiphenyl	10.0 ng/mL

Individual Standard Mixture B	Low Point Concentration
beta-BHC	5.0 ng/mL
delta-BHC	5.0 ng/mL
Aldrin	5.0 ng/mL
Heptachlor expoxide	5.0 ng/mL
alpha-Chlordane	5.0 ng/mL
gamma-Chlordane	5.0 ng/mL
p,p'-DDE	10.0 ng/mL
Endosulfan sulfate	10.0 ng/mL
Endrin aldehyde	10.0 ng/mL
Endrin ketone	10.0 ng/mL
Endosulfan II	10.0 ng/mL
Tetrachloro-m-xylene	5.0 ng/mL
Decachlorobiphenyl	10.0 ng/mL

2.2 The standards are to be analyzed using the following gas chromatographic analytical conditions. The conditions are recommended unless otherwise noted.

Carrier Gas:	Helium
Column Flow:	5 mL/min
Make-up Gas:	P-5/P-10 or N2 (required)
Injector Temperature:	> 200°C (see 4.2)
Injection:	On-column
Injection Volume:	1 or 2 µL (see 4.1)
Injector:	Grob-type, splitless
Initial Temperature:	150°C
Initial Hold Time:	1/2 min
Temperature Ramp:	5°C to 6°C/min
Final Temperature:	275°C
Final Hold Time:	Until after Decachlorobiphenyl has eluted (approximately 10 minutes)

Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, and MS/MSDs.

The linearity of the ECD may be greatly dependent on the flow rate of the make-up gas. Care must be taken to maintain stable and appropriate flow of make-up gas to the detector.

2.3 Initial Calibration Sequence

2.3.1 Before any samples are analyzed, it is necessary for the Laboratory to complete the initial calibration sequence given below.

2.3.2 Samples may be analyzed only after the initial calibration acceptance criteria (Paragraph 2.4) are met. Otherwise, the analytical system is not functioning adequately for use with this Protocol.

2.3.3 The initial calibration may continue to be used as long as the analytical system remains under control. The proof that the analytical system is under control is provided by the analyses of the Performance Evaluation Mixtures. If those analyses do not meet the criteria described in paragraph 7, appropriate corrective action must be taken, and the initial calibration sequence must be repeated. The calibration sequence must also be repeated if any major change in instrument hardware or instrument parameters is made (e.g., if a new column is installed or if the detector temperature is changed).

***NOTE**: Steps 16 and 17 are used as part of the calibration verification as well (see paragraph 7).*

INITIAL CALIBRATION SEQUENCE

1. Resolution Check
2. Performance Evaluation Mixture
3. Aroclor 1016/1260
4. Aroclor 1221
5. Aroclor 1232
6. Aroclor 1242
7. Aroclor 1248
8. Aroclor 1254
9. Toxaphene
10. Low Point Standard A
11. Low Point Standard B
12. Midpoint Standard A
13. Midpoint Standard B
14. High Point Standard A
15. High Point Standard B
16. Instrument Blank
17. Performance Evaluation Mixture

2.4 Initial Calibration Acceptance Criteria (apply to each GC column independently)

2.4.1 The initial calibration sequence must be analyzed in the order listed in Paragraph 2.3 using the optimized GC/EC operating conditions described in Paragraph 2.2. The standards must be prepared according to Paragraph 2.1. Calculate the calibration factors and retention times as follows:

2.4.1.1 During the initial calibration sequence, the Laboratory must establish the magnitude of the linear ECD response range for each single component pesticide and surrogate on each column and for each GC system. This is accomplished by analyzing the Individual Standard Mixtures A and B at three concentrations during the initial calibration sequence in paragraph 6.

2.4.1.2 The linearity of the instrument is determined by calculating a percent relative standard deviation (%RSD) of the calibration factors from a three-point calibration curve for each single component pesticide and surrogate. Either peak area or peak height may be used to calculate calibration factors used in the %RSD equation. For example, it is permitted to calculate linearity for Endrin based on peak area and to calculate linearity for Aldrin based on peak height. It is not permitted within a %RSD calculation for an analyte to use calibration factors calculated from both peak area and peak height. For example, it is <u>not</u> permitted to calculate the calibration factor for the low point standard for endrin using peak height and calculate the midpoint and high point standard calibration factors for endrin using peak area.

2.4.1.3 Calculate the calibration factor for each single component pesticide and surrogate over the initial calibration range using

Equation 1. The calibration factors for the surrogates are calculated from the three analyses of Individual Standard Mixture A only.

2.4.1.4 Calculate the mean and the %RSD of the calibration factors for each single component pesticide and surrogate over the initial calibration range using Equations 1 and 2.

Equation 1.

$$CF = \frac{\text{Peak Area (or Height) of the Standard}}{\text{Mass Injected (ng)}}$$

Where:

CF = Calibration Factor

Equation 2.

$$\overline{CF} = \sum_{i=1}^{n} \frac{CF_i}{n}$$

2.4.2 The resolution criterion is that the depth of the valley between two adjacent peaks in the Resolution Check Mixture must be greater than or equal to 60.0% of the height of the shorter peak. The poorest resolution on the DB-608 column probably will be between DDE and Dieldrin, between Methoxychlor and Endrin ketone and between Endosulfan I and gamma-Chlordane. On the DB-1701 column, resolution difficulties most frequently occur between Endosulfan I and gamma-Chlordane, and between Methoxychlor and Endosulfan sulfate.

2.4.3 All peaks in both of the Performance Evaluation Mixtures must be 100 percent resolved on both columns.

2.4.4 The absolute retention times of each of the single component pesticides and surrogates in both of the PEMs must be within the retention time windows determined from the three-point initial calibration, in paragraph 2.4.

2.4.5 The relative percent difference of the calculated amount and the true amount for each of the single component pesticides and surrogates in both of the PEMs must be less than or equivalent to 25.0 percent, using Equation 2.

2.4.6 At least one chromatogram from each of the two Individual Standard Mixtures A and B, run during the initial calibration, must yield peaks that give recorder deflections of 50 to 100 percent of full scale.

2.4.7 The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.

2.4.8 The % RSD of the calibration factors for each single compound target compound must be less than or equal to 20.0 percent, except as noted below. The % RSD of the calibration factors for the two surrogates must be less than or equal to 30.0 percent. Up to two single component target compounds (but not surrogates) per column may exceed the 20.0 percent limit for %RSD, but those compounds must have a % RSD of less than or equal to 30.0 percent.

Equation 2.

$$\% \text{ RSD} = \frac{\text{Standard Deviation}}{\overline{CF}} \times 100$$

Where:

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2}{n - 1}}$$

Where:

x_i = each individual value used to calculate the mean

$\overline{x}$ = the mean of n values

n = the total number of values

2.4.8.1 The linearity of the calibration is considered acceptable when the % RSD of the three point calibration is less than 20.0 percent except as noted in the following.

The % RSD of the two surrogates must be less than or equal to 30.0 percent. Up to two single compound target compounds (but not surrogates) per column may exceed the 20.0 percent limit for % RSD., but those compounds must have a % RSD of less than or equal to 30.0 percent.

2.4.8.2 If the linearity requirements listed above are met, the calibration factor from the mid point concentration standard is used for quantitation of each single component pesticide.

2.4.9 The breakdown of DDT and Endrin in both of the Performance Evaluation Mixtures must be less than 20.0 percent, and the combined breakdown of DDT and Endrin must be less than 30.0 percent where,

Equation 3.

$$\% \text{ Breakdown DDT} = \frac{\text{Amount found in ng (DDD+DDE)}}{\text{Amount in ng of DDT injected}} \times 100$$

Equation 4.

$$\% \text{ Breakdown Endrin} = \frac{\text{Amount found in ng (Endrin aldehyde + Endrin ketone)}}{\text{Amount of Endrin injected in ng}} \times 100$$

Equation 5.

$$\text{Combined \% Breakdown} = \%\text{Breakdown DDT} + \%\text{Breakdown Endrin}$$

2.4.10 Toxaphene and Aroclors require only a single-point calibration and they present special analytical difficulties. Because of the alteration of these materials in the environment, it is probable that samples which contain multicomponent analytes will give patterns similar to, but not identical with, those of the standards.

2.4.11 A set of three to five major peaks is selected for each multicomponent analyte. Retention times and calibration factors are determined from the initial calibration analysis for each peak. Guidance for the choice of which peaks to use is given as follows:

2.4.11.1 The choice of the peaks used for multicomponent quantitation and the recognition of those peaks may be complicated by the environmental alteration of the Toxaphene or Aroclors, and by the presence of coeluting analytes or matrix interferences, or both.

2.4.11.2 If more than one multicomponent analyte is observed in a sample, the Laboratory must choose separate peaks to quantitate the different multicomponent analytes. A peak common to both analytes present in the sample must not be used to quantitate either compound.

2.4.12 Sample analysis may not proceed until a satisfactory calibration has been demonstrated.

2.5 The documentation includes Form VI PEST, chromatograms and data system printouts of all standards for the pesticide/Aroclor calibration standards.

Section 3. -- GC/EC Continuing Calibration For Target Compounds And Surrogates.

Once the GC/EC system has been calibrated, the calibration must be verified each twelve (12) hour time period for each GC column and instrument used for analysis. The calibration is verified through the analysis of instrument blanks, Performance Evaluation Mixtures (PEM), and the mid point concentrations of Individual Standard Mixtures A and B.

3.1 Three types of analyses are used to verify the calibration and evaluate instrument performance. The analyses of instrument blanks, Performance Evaluation Mixtures (PEM), and the mid point concentration of Individual Standard Mixtures A and B constitute the continuing calibration. Sample data are not acceptable unless bracketed by acceptable analyses of instrument blanks, PEM, and both Individual Standard Mixtures A and B. The Performance Evaluation Mixtures and the Individual Standard Mixtures A and B are prepared as described in Paragraphs 1. and 2.

3.2 Instrument blank

3.2.1 An instrument blank is a hexane or iso-octane solution containing 20.0 ng/mL of tetrachloro-m-xylene and decachlorobiphenyl.

3.2.2 The first analysis in a 12-hour analysis sequence must be an instrument blank. All acceptable sample analyses are to be bracketed by acceptable instrument blanks, as described in Paragraph 3.3.

3.3 All acceptable samples must be analyzed within a valid analysis sequence as given below.

3.3.1 An acceptable instrument blank must be analyzed within a 12-hour analysis sequence and must demonstrate that no analyte in Exhibit C is detected at greater than 0.5 times the CRQL and that the surrogate retention times are within the retention time windows. For comparing the results of the instrument blank analysis to the CRQLs, assume that the material in the instrument resulted from the extraction of a 1 L water sample and calculate the concentration of each analyte using Equation 6. Compare the results to <u>one-half</u> the CRQL values for water samples in Exhibit C.

Equation 6.

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(Df)}{(CF)(V_o)(V_i)}$$

Where:

A_x = Area of the peak for the compound to be measured

CF = Calibration factor for the mid point concentration external standard (area per ng)

V_o = Volume of water extracted in milliliters (mL)

V_i = Volume of extract injected in microliters (µL). (If a single injection is made onto two columns, use one half the volume in the syringe as the volume injected onto to each column.)

V_t = Volume of the concentrated extract in microliters (µL) (this volume must be 10,000 µL)

Df = Dilution Factor. The dilution factor for analysis of water samples by this method is defined as follows:

$$Df = \frac{\text{µL most conc. extract used to make dilution + µL clean solvent}}{\text{µL most conc. extract used to make dilution}}$$

If no dilution is performed, Df = 1.0.

3.3.2 If analytes are detected at greater than half the CRQL, or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. After an acceptable instrument blank is run, all samples which were run after the last acceptable instrument blank must be reinjected during a valid run sequence at no additional cost to the NYSDEC and must be reported.

3.3.3 Analysts are cautioned that running an instrument blank once every 12 hours is the minimum Protocol requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable, and will result in the rejection of data. Therefore, it may be necessary to run instrument blanks more often to avoid discarding data.

Time	Injection #	Material Injected
	1 - 15	First 15 steps of the initial calibration
0 hr.	16	Instrument blank at end of initial calibration
	17	PEM at end of initial calibration
	18	First sample
	0	Subsequent samples
	0	
	0	
12 hr.	0	Last sample
	1st injection past	Instrument blank
	12:00 hr.	
	2nd and 3rd	Individual Standard Mixtures
	injections past	A and B
	12:00 hr.	
	0	Sample
	0	
	0	
	0	Subsequent samples
	0	
Another 12 hr.	0	Last sample
	1st injection past	Instrument blank
	12 hr.	
	2nd injection	PEM
	0	Sample
	0	
	0	Subsequent samples
	0	

Time	Injection #	Material Injected
Another 12 hr.	0	Last sample
	1st injection past 12:00 hr.	Instrument blank
	2nd and 3rd injections past 12:00 hr.	Individual Standard Mixtures A and B
	0	Sample
	0	
	0	
	0	Subsequent samples
	0	
	etc.	

***NOTE**: The first 12 hours are counted from the injection #16 (the Instrument Blank at the end of the initial calibration sequence), not from injection #1. Samples may be injected until 12:00 hours have elapsed. All subsequent 12-hour periods are timed from the injection of the instrument blank that brackets the front end of the samples. Because the 12-hour time period is timed from injection of the instrument blank until the injection of the last sample, each 12-hour period may be separated by the length of one chromatographic run, that of the analysis of the last sample. While the 12-hour period may not be exceeded, the Laboratory may run instrument blanks and standards more frequently, for instance to accommodate staff working on 8-hour shifts.*

3.4 An instrument blank and the Performance Evaluation Mixture must bracket one end of a 12-hour period during which sample data are collected, and a second instrument blank and the mid point concentration of Individual Standard Mixtures A and B must bracket the other end of the 12-hour period.

3.5 For the 12-hour period immediately following the initial calibration sequence, the instrument blank and the PEM that are the last two steps in the initial calibration sequence bracket the front end of that 12-hour period. The injection of the instrument blank starts the beginning of that 12-hour period. Samples may be injected for 12 hours from the injection of the instrument blank. The three injections immediately after that 12-hour period must be an instrument blank, Individual Standard Mixture A, and Individual Standard Mixture B. The instrument blank must be analyzed first, before either standard. The Individual Standard Mixtures may be analyzed in either order (A,B or B,A).

3.6 The analyses of the instrument blank and Individual Standard Mixtures A and B immediately following one 12-hour period may be used to begin the subsequent 12-hour period, provided that they meet the acceptance criteria. In that instance, the subsequent 12-hour period must be bracketed by the acceptable analyses of an instrument blank and a PEM, in that order. Those two analyses may in turn be used to

bracket the front end of yet another 12-hour period. This progression may continue every 12 hours until such time as any of the instrument blanks, PEMs, or Individual Standard Mixtures fails to meet the acceptance criteria. The 12-hour time period begins with the injection of the instrument blank. Standards (PEM or Individual Standard Mixtures), samples and required blanks may be injected for 12:00 hours from the time of injection of the instrument blank.

3.7 If more than 12 hours have elapsed since the injection of the instrument blank that bracketed a previous 12-hour period, an acceptable instrument blank and PEM must be analyzed in order to start a new sequence. This requirement applies even if no analyses were performed since that standard(s) was injected.

3.8 After a break in sample analyses, the Laboratory may only resume the analysis of samples using the current initial calibration for quantitation by analyzing an acceptable instrument blank and a PEM.

3.9 If the entire 12-hour period is not required for the analyses of all samples to be reported and all data collection is to be stopped, the incomplete sequence must be ended with either the instrument blank/PEM combination or the instrument blank/Individual Standard Mixtures A and B combination, whichever was due to be performed at the end of 12-hour period.

3.10 Analysts are cautioned that running an instrument blank and a performance evaluation mixture once every 12 hours is the minimum contract requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks and performance evaluation mixtures more often to avoid discarding data.

3.11 The requirements for running the instrument blanks, Performance Evaluation Mixture, and Individual Standard Mixtures A and B are waived when no samples, method blanks, or matrix spikes are run during that 12-hour period. After a break in sample analysis, the Laboratory may resume the analysis of samples, method blanks, and matrix spikes and may use the current initial calibration for quantitation only after an acceptable PEM is run. If a successful PEM cannot be run after an interruption, an acceptable initial calibration must be run before sample data may be collected. All acceptable sample analyses must be bracketed by acceptable performance evaluation mixtures and instrument blanks.

3.12 Technical Acceptance Criteria (apply to each GC column independently)

3.12.1 All single component pesticides and surrogates in the Performance Evaluation Mixtures used to demonstrate continuing calibration must be 100 percent resolved. The resolution between any two adjacent peaks in the midpoint concentrations of Individual Standard Mixtures A and B in the initial calibration must be greater than or equal to 90.0 percent.

3.12.2 The absolute retention time for each of the single component pesticides and surrogates in the PEMs and mid point concentration of the Individual Standard Mixtures used to demonstrate continuing calibration must be within the retention time window determined from the three-point initial calibration.

3.12.3 The relative percent difference of the calculated amount and the true amount for each of the single component pesticides and surrogates in the PEM and mid point concentration of the Individual Standard Mixtures used to demonstrate continuing calibration must be less than or equal to 25.0 percent, using Equation 7.

Equation 7.

$$RPD = \frac{|C_{nom} - C_{calc}|}{C_{nom}} \times 100$$

C_{nom} = true concentration of each analyte

C_{calc} = calculated concentration of each analyte from the analyses of the standard

***Note**: The vertical bars in the equation indicate the absolute value, hence RPD is always a positive number.*

3.12.4 The percent breakdown of DDT and Endrin in the PEM must be less than or equal to 20.0 percent on both columns. The combined breakdown of DDT and Endrin must be less than or equal to 30.0 percent on both columns.

3.12.5 All instrument blanks must meet the acceptance criteria in Paragraph 7.4.

3.13 The continuing calibration is evaluated on the basis of the stability of the retention times of the target compounds in the standards.

3.14 The continuing calibration is evaluated on the basis of the stability of the instrument response to the target compounds in the PEM, as judged by the reproducibility of the determinations of the concentrations of these compounds in the standard.

3.15 The continuing calibration is evaluated on the basis of the extent of breakdown of two target compounds in the PEM, Endrin and 4,4'-DDT, as described in Paragraph 2.4.9.

3.16 The continuing calibration is evaluated on the basis of the levels of contamination that are found in the instrument blank.

3.16.1 An acceptable instrument blank must be analyzed within a 12-hour analysis sequence and must demonstrate that no analyte in Exhibit C is detected at greater than 0.5 times the CRQL and that the surrogate retention times are within the retention time windows. For comparing the results of the instrument blank analysis to the CRQLs, assume that the material in the instrument resulted from the extraction of a 1 L water sample and calculate the concentration of each analyte using the equation in Paragraph 3.3.1. Compare the results to <u>one-half</u> the CRQL values for water samples in Exhibit C.

3.16.2 If analytes are detected at greater than half the CRQL, or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. After an acceptable instrument blank is run, all samples which were run after the last acceptable instrument blank must be reinjected during a valid run sequence at no additional cost to the NYSDEC and must be reported.

3.17 The documentation includes Form VII PEST, Form VIII PEST, chromatograms and data system printouts for all standards and instrument blanks analyzed.

Section 4. -- Determination of Retention Times and Retention Time Windows

The identification of single component pesticides by gas chromatographic methods is based primarily on retention time data. The identification of multicomponent analytes is based primarily on recognition of patterns of retention times displayed on a chromatogram. Therefore, the determination of retention times and retention time windows is crucial to the provision of valid data for these target compounds.

4.1 The identification of all Pesticide/Aroclor target compounds analyzed by the procedures described in Exhibit D, is based on the use of absolute retention time. The mean retention time of each target compound, or each peak in a multicomponent target compound, is determined from the initial calibration standards, according to Equation 8.

Equation 8.

$$\overline{RT} = \sum_{i=1}^{3} \frac{RT_i}{3}$$

Section 5. -- Determination of Absolute Retention Times.

5.1 During the initial calibration sequence, absolute retention times (RT) are determined for all single response pesticides, the surrogates, and at least three major peaks of each multicomponent analyte.

5.2 For single component pesticides, an RT is measured in each of three calibration standards and the mean RT is calculated as the average of the three values. An RT is measured for the surrogates in each of the three analyses of Individual Mixture A during the initial calibration and the mean RT is calculated as the average of the three values using Equation 9. above.

5.3 A retention time window is calculated for each single component analyte and surrogate by using the list in Paragraph 5.8. Windows are centered around the mean absolute retention time for the analyte established during the initial calibrations.

5.4 For each multicomponent analyte, the RTs for three to five peaks are calculated from the initial calibration standard analysis. An RT window of ±0.07 minutes is used for all multicomponent analyte peaks.

5.5 Analytes are identified when peaks are observed in the RT window for the compound on both GC columns.

5.6 The retention time shifts of the surrogates are used to evaluate the stability of the gas chromatographic system during analysis of samples and standards. The retention time of the surrogates must be within the retention time windows determined in Paragraphs 5.3.

5.7 The documentation includes Form VI PEST, Form VII PEST, Form VIII PEST, chromatograms and data system printouts for all standards for the Pesticide/Aroclor initial and continuing calibrations, on each instrument and GC column used for analysis.

5.8 Retention time windows for single and multicomponent analytes and surrogates.

Compound	Retention Time Window in Minutes
alpha-BHC	±0.05
beta-BHC	±0.05
gamma-BHC	±0.05
delta-BHC	±0.05
Heptachlor	±0.05
Aldrin	±0.05
alpha-Chlordane	±0.07
gamma-Chlordane	±0.07
Heptachlor epoxide	±0.07
Dieldrin	±0.07
Endrin	±0.07
Endrin aldehyde	±0.07
Endrin ketone	±0.07
DDD	±0.07
DDE	±0.07
DDT	±0.07
Endosulfan I	±0.07
Endosulfan II	±0.07
Endosulfan sulfate	±0.07
Methoxychlor	±0.07
Aroclors	±0.07
Toxaphene	±0.07
Tetrachloro-m-xylene	±0.05
Decachlorobiphenyl	±0.10

Section 6. -- Analytical Sequence

6.1 The standards and samples analyzed according to the procedures in Exhibit D must be analyzed in a sequence described in Paragraph 3.3. This sequence includes requirements that apply to the initial and continuing calibrations, as well as to the analysis of samples. The documentation includes Form VIII PEST.

6.2 Before any samples are analyzed, it is necessary for the Laboratory to complete an acceptable initial calibration sequence (see Paragraph 2).

6.3 After the initial calibration, the analysis sequence may continue as long as acceptable instrument blanks, Performance Evaluation Mixtures, and Individual Standard Mixtures A and B are analyzed at the required frequency (see Paragraph 1). This analysis sequence shows only the minimum required blanks and standards. More blanks and standards may be run at the discretion of the Laboratory; these must also satisfy the criteria presented in paragraph 7 in order to continue the run sequence.

6.4 An analysis sequence must also include all required matrix spike/matrix spike duplicate/matrix spike blank analyses and method blanks, but the Laboratory may decide at what point in the sequence they are to be analyzed.

6.5 A standard of any identified Aroclor must be run within 72 hours of its detection in a sample chromatogram.

Section 7. -- Blank Analysis

There are three types of blanks always required by this method: the method blank, the matrix spike blank, and the instrument blank. A separate sulfur cleanup blank may be required if all samples associated with a given method blank are not subjected to sulfur cleanup. Samples that are associated with a sulfur cleanup blank are also associated with the method blank with which they were extracted. Both the method and sulfur cleanup blanks must meet the respective acceptance criteria for the sample analysis acceptance criteria to be met.

7.1 Method blank

7.1.1 Method blanks are spiked with the surrogate solution, extracted, cleaned up, and analyzed by following the same procedure that is used with the samples. A water method blank is one liter of reagent water treated as the water sample aliquot. A soil method blank is 30 g of sodium sulfate treated as the soil sample aliquot.

Method blank analysis must be performed once for the following, whichever is most frequent, and analyzed on each GC/EC system used to analyze samples:

- Each SDG, OR
- Each 7 calendar day period during which samples in an SDG are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), OR

- Each 20 samples in an SDG, including matrix spikes and re-analyses, OR

- Whenever samples are extracted by the same procedure (separatory funnel or continuous liquid-liquid extraction).

7.1.2 In order to be acceptable, a method blank analysis cannot contain any of the analytes listed in Exhibit C at greater than the CRQL. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl.

7.1.3 All samples associated with an unacceptable method blank (see Form IV) must be reextracted and reanalyzed at no additional cost to the NYSDEC.

7.2 Matrix Spike Blank

7.2.1 Matrix spike blanks are spiked with the surrogate solution and the matrix spiking solution, extracted, cleaned up, and analyzed by following the same procedure that is used with the samples. A matrix spike blank is one liter of reagent water treated as the water sample aliquot.

Matrix spike blank analysis must be performed once for each matrix spike/matrix spike duplicate analysis (see Paragraph 9.)

7.2.2 In order to be acceptable, a matrix spike blank analysis must meet the recovery limits below. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl.

MATRIX SPIKE BLANK RECOVERY LIMITS

Compound	%Recovery
gamma-BHC (Lindane)	56-123
Heptachlor	40-131
Aldrin	40-120
Dieldrin	52-126
Endrin	56-121
4,4'-DDT	38-127

7.2.3 All samples associated with an unacceptable matrix spike blank (see Form IV) must be reextracted and reanalyzed at no additional cost to the NYSDEC.

7.3 Sulfur Cleanup Blank.

7.3.1 The sulfur cleanup blank is a modified form of the method blank. The sulfur cleanup blank is hexane spiked with the surrogates and passed through the sulfur cleanup procedure.

7.3.2 The sulfur cleanup blank is prepared when only part of a set of samples extracted together requires sulfur removal. A method blank is associated with the entire set of samples. The sulfur cleanup blank is associated with the part of the set which required sulfur cleanup. If all the samples associated with a given method blank are subjected to sulfur cleanup, then the method blank must be subjected to sulfur cleanup, and no separate sulfur cleanup blank is required.

7.3.3 In order to be acceptable, a sulfur blank analysis cannot contain any of the analytes listed in Exhibit C at greater than the CRQL, assuming that the material in the sulfur blank resulted from the extraction of a 1 L water sample. Calculate the concentration of each analyte using the equation in Paragraph 3.3.1. Compare the results to the CRQL values for water samples in Exhibit C. The surrogate retention times must be within the retention time windows calculated from the initial calibration sequence mean retention time for both tetrachloro-m-xylene and decachlorobiphenyl.

7.3.4 All samples associated with an unacceptable sulfur blank (see Form IV) must be reextracted and reanalyzed at no additional cost to the NYSDEC.

7.4 Instrument blank

7.4.1 An instrument blank is a hexane or iso-octane solution containing 20.0 ng/mL of tetrachloro-m-xylene and decachlorobiphenyl.

7.4.2 The first analysis in a 12-hour analysis sequence must be an instrument blank. All acceptable samples analyses are to be bracketed by acceptable instrument blanks, as described in Paragraph 3.2.

7.4.3 An acceptable instrument blank must be analyzed within a 12-hour analysis sequence and must demonstrate that no analyte in Exhibit C is detected at greater than 0.5 times the CRQL and that the surrogate retention times are within the retention time windows. For comparing the results of the instrument blank analysis to the CRQLs, assume that the material in the instrument resulted from the extraction of a 1 L water sample and calculate the concentration of each analyte using the equation in Paragraph 3.3.1. Compare the results to <u>one-half</u> the CRQL values for water samples in Exhibit C.

7.4.4 If analytes are detected at greater than half the CRQL, or the surrogate RTs are outside the RT windows, all data collection must be stopped, and corrective action must be taken. Data for samples which were run between the last acceptable instrument blank and the unacceptable blank are considered suspect. An acceptable instrument blank must be run before additional data are collected. After an acceptable instrument blank is run, all samples which were run

after the last acceptable instrument blank must be reinjected during a valid run sequence at no additional cost to the NYSDEC and must be reported.

7.4.5 Analysts are cautioned that running an instrument blank once every 12 hours is the minimum Protocol requirement. Late eluting peaks may carry over from one injection to the next if highly complex samples are analyzed or if the GC conditions are unstable. Such carryover is unacceptable. Therefore, it may be necessary to run instrument blanks more often to avoid discarding data.

Section 8. -- Surrogate Recoveries

The recoveries of the two surrogates are calculated from the analysis on each GC column of each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank. The purpose of the surrogates is to evaluate the preparation and analysis of samples.

8.1 The surrogates are added to each sample, blank, matrix spike, matrix spike duplicate, and matrix spike blank prior to extraction, at the concentrations described below.

8.1.1 Surrogate solution - the surrogates, Tetrachloro-m-xylene and Decachlorobiphenyl, are added to all standards, samples, matrix spikes, and blanks. Prepare a surrogate spiking solution of 0.2 µg/mL of each of the two compounds in acetone. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner, if comparison with quality control check samples indicates a problem.

***CAUTION**: Analysts must allow all spiking solutions to equilibrate to room temperature before use.*

8.2 The concentrations of the surrogates are calculated separately for both GC columns in a similar manner as the other analytes, using Equations 10 and 11. Use the calibration factors from the midpoint concentration of Individual Standard Mixture A. The recoveries of the surrogates are calculated for both GC columns according to Equation 9.

Equation 9.

$$\text{Surrogate Percent Recovery} = \frac{Q_d}{Q_a} \times 100$$

Where,

Q_d = Quantity determined by analysis

Q_a = Quantity added to sample/blank

The limits for the recovery of the surrogates are 30 - 150 percent for both surrogate compounds. As these limits are only advisory, no further action is required by the

Laboratory is required, however, frequent failures to meet the limits for surrogate recovery warrant investigation by the Laboratory, and may result in questions from the NYSDEC. Surrogate recovery data from both GC columns are reported (see Exhibit B).

8.3 The quality control limits for surrogate recovery are 30-150 percent. These limits are only advisory, and no further action by the Laboratory is required if the limits are exceeded, however, frequent failures to meet the limits for surrogate recovery warrant investigation by the Laboratory, and any result in questions from the NYSDEC.

8.4 The documentation includes Form II PEST, a chromatogram and a GC/EC data system printout for the analysis of each sample, blank, matrix spike, and matrix spike duplicate.

Section 9. -- Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank Analysis

In order to evaluate the effects of the sample matrix on the methods used for pesticide/Aroclor analyses, the NYSDEC has prescribed a mixture of pesticide/Aroclor target compounds to be spiked into two aliquots of a sample, and one aliquot of reagent water and analyzed in accordance with the appropriate method.

9.1 A matrix spike and matrix spike duplicate must be extracted and analyzed at least once with every 20 samples of each matrix.

***NOTE**: There is no differentiation between "low" and "medium" soil samples in this method. Therefore only one soil MS/MSD is to be submitted per SDG.*

9.2 The percent recoveries and the relative percent difference between the recoveries of each of the 6 compounds in the matrix spike blank and samples will be calculated and reported by using the following equations:

Equation 10.

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike sample result

SR = Sample result

SA = Spike added

Equation 11.

$$RPD = \frac{|MSR - MSDR|}{1/2(MSR + MSDR)} \times 100$$

Where,

RPD = Relative percent difference

MSR = Matrix spike recovery

MSDR = Matrix spike duplicate recovery

The vertical bars in the formula above indicate the absolute value of the difference, hence RPD is always expressed as a positive value.

9.3 The Laboratory shall report matrix spike and matrix spike duplicate recoveries and percent difference values with the analytical results (see Exhibit B). The limits for matrix spike compound recovery and RPD are given below. As these limits are only advisory, no further action by the Laboratory is required, however, frequent failures to meet the limits for recovery or RPD warrant investigation by the Laboratory, and may result in questions from the NYSDEC.

MATRIX SPIKE RECOVERY AND
RELATIVE PERCENT DIFFERENCE LIMITS

Compound	%Recovery	RPD
gamma-BHC (Lindane)	56-123	15
Heptachlor	40-131	20
Aldrin	40-120	22
Dieldrin	52-126	18
Endrin	56-121	21
4,4'-DDT	38-127	27

9.4 The documentation includes Form I PEST for both the MS and MSD analyses, Form III PEST, and chromatograms and a GC/EC data system printout for each analysis.

Section 10. -- Dilution of Samples, Matrix Spikes, Matrix Spike Duplicates, and Matrix Spike Blanks

If the on-column concentration of any sample exceeds the initial calibration range, that sample must be diluted and reanalyzed, as described below. Guidance in performing dilutions and exceptions are given in that paragraph, and reiterated here.

10.1 In order to be quantitated, the detector response (peak area or peak height) of all of the single component analytes must lie between the response of the low and high concentrations in the initial calibration. If the analytes are detected below the CRQL, they are reported as present below the CRQL, and flagged according to the instructions in Exhibit B. If they are detected at a level greater than the high calibration point, the sample must be diluted either to a maximum of 1:5 or until the response is within the linear range established during calibration. Guidance in performing dilutions and exceptions to this requirement are given below.

10.1.1 If the response is still above the high calibration point after the dilution of 1:5, the Laboratory shall contact the BWAR or Project Director immediately.

10.1.2 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

10.1.3 The dilution factor chosen should keep the response of the largest peak for a target compound in the upper half of the initial calibration range of the instrument.

10.1.4 Do not submit data for more than two analyses, i.e., the original sample extract and one dilution, or, if a screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

10.1.5 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis and note the problem in the SDG Narrative.

10.2 f the response is still above the high calibration point after the dilution of 1:5, the Laboratory shall contact the BWAR immediately.

10.3 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

10.4 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

10.5 Do not submit data for more than two analyses, i.e., the original sample and one dilution, or, if the pesticide/Aroclor screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

10.6 Do not dilute MS/MSD samples to get either spiked or non-spiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis and note the problem in the SDG Narrative. MSB SAMPLES MUST NEVER BE DILUTED.

Part XII -- Analytical Standards Requirements

Overview

Neither the U.S. Environmental Protection NYSDEC nor the New York State Department of Environmental Conservation will supply analytical reference standards either for direct analytical measurements or for the purpose of traceability. All contract laboratories will be required to prepare from neat materials or purchase from private chemical supply houses those standards necessary to successfully and accurately perform the analyses required in this Protocol.

Section 1. -- Preparation of Chemical Standards from the Neat High Purity Bulk Material

A laboratory may prepare their chemical standards from neat materials. Commercial sources for neat chemical standards pertaining to compounds listed on the Compound Target List are given in the Appendix C of the "Quality Assurance Materials Bank: Analytical Reference Standards" Seventh Edition, January 1988. Laboratories should obtain the highest purity possible when purchasing neat chemical standards; standards purchased at less than 97% purity must be documented as to why a higher purity could not be obtained.

1.1 Neat chemical standards must be kept refrigerated when not being used in the preparation of standard solutions. Proper storage of neat chemicals is essential in order to safeguard them from decomposition.

1.2 The purity of a compound can sometimes be misrepresented by a chemical supply house. Since knowledge of purity is needed to calculate the concentration of solute in a solution standard, it is the Laboratory's responsibility to have analytical documentation ascertaining that the purity of each compound is correctly stated. Purity confirmation, when performed, should use either differential scanning calorimetry, gas chromatography with flame ionization detection, high performance liquid chromatography, infrared spectrometry, or other appropriate techniques. Use of two or more independent methods is recommended. The correction factor for impurity when weighing neat materials in the preparation of solution standards is:

Equation 1.

$$\text{weight of impure compound} = \frac{\text{weight of pure compound}}{(\text{percent purity}/100)}$$

where "weight of pure compound" is that required to prepare a specific volume of a solution standard of a specified concentration.

1.3 Mis-identification of compounds occasionally occurs and it is possible that a mislabeled compound may be received from a chemical supply house. It is the Laboratory's responsibility to have analytical documentation ascertaining that all compounds used in the preparation of solution standards be correctly identified. Identification confirmation, when performed, should use , gas chromatographic/mass

spectrometry analysis on at least two different analytical columns, or other appropriate techniques.

1.4 Calculate the weight of material to be weighed out for a specified volume taking into account the purity of the compound and the desired concentration. A second person must verify the accuracy of the calculations. Check balances for accuracy with a set of standard weights. All weighing should be performed on an analytical balance to the nearest 0.1 mg and verified by a second person. The solvent used to dissolve the solute should be compatible with the protocol in which the standard is to be used; the solute should be soluble, stable, and non-reactive with the solvent. In the case of a multicomponent solution, the components must not react with each other.

1.5 Transfer the solute to a volumetric flask and dilute to the specified solution volume with solvent after ensuring dissolution of the solute in the solvent. Sonication or warming may be performed to promote dissolution of the solute. This solution is to be called the primary standard and all subsequent dilutions must be traceable back to the primary standard.

1.6 Log notebooks are to be kept for all weighing and dilutions. All subsequent dilutions from the primary standard and the calculations for determining their concentrations are to be recorded and verified by a second person. All solution standards are to be refrigerated when not in use. All solution standards are to be clearly labeled as to the identity of the compound or compounds, concentration, date prepared, solvent, and initials of the preparer.

Section 2. -- Purchase Of Chemical Standards Already In Solution

Solutions of analytical reference standards can be purchased by Laboratories provided they meet the following criteria:

2.1 Laboratories must maintain the following documentation to verify the integrity of the standard solutions they purchase:

2.1.1 mass spectral identification confirmation of the neat material

2.1.2 purity confirmation of the neat material

2.1.3 chromatographic and quantitative documentation that the solution standard was QC checked according to the following section

2.2 The Laboratory must purchase standards for which the quality is demonstrated statistically and analytically by a method of the supplier's choice. One way this can be demonstrated is to prepare and analyze three solutions; a high standard, a low standard, and a standard at the target concentration (see parts a and b below). The supplier must then demonstrate that the analytical results for the high standard and low standard are consistent with the difference in theoretical concentrations. This is done by the Student's t-test in paragraph 2.3.4. If this is achieved, the supplier must then demonstrate that the concentration of the target standard lies midway between the concentrations of the low and high standards. This is done by the Student's t-test in paragraph 2.3.5. Thus the standard is certified to be within 10 percent of the target concentration.

If the procedure above is used, the supplier must document that the following have been achieved:

2.2.1 Two solutions of identical concentration must be prepared independently from neat materials. An aliquot of the first solution must be diluted to the intended concentration (the "target standard"). One aliquot is taken from the second solution and diluted to a concentration ten percent greater than the target standard. This is called the "high standard". One further aliquot is taken from the second solution and diluted to a concentration 10 percent less that the target standard. This is called the "low standard".

2.2.2 Six replicate analyses of each standard (a total of 18 analyses) must be performed in the following sequence: low standard, target, high standard, low standard, target standard, high standard, ...

2.2.3 The mean and variance of the six results for each solution must be calculated.

Equation 2.

$$\text{MEAN} = \frac{(Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6)}{6}$$

Equation 3.

$$\text{VARIANCE} = \frac{(Y_1^2 + Y_2^2 + Y_3^2 + Y_4^2 + Y_5^2 + Y_6^2 - (6*\text{MEAN})^2)}{5}$$

The values Y_1, Y_2, Y_3, ..., represent the results of the six analyses of each standard. The means of the low, target, and high standards are designated M_1, M_2, and M_3, respectively. The variances of the low, target, and high standards are designated V_1, V_2, and V_3, respectively. Additionally, a pooled variance, V_p, is calculated.

Equation 4.

$$V_p = \frac{\left(\frac{V_1}{0.81}\right) + V_2 + \left(\frac{V_3}{1.21}\right)}{3}$$

If the square root of V_p is less than one percent of M_2, then $M_2^2/10{,}000$ is to be used as the value of V_p in all subsequent calculations.

2.2.4 The test statistic must be calculated:

Equation 5.

$$\text{TEST STATISTIC} = \frac{\left| \frac{M_3}{1.1} - \frac{M_1}{0.9} \right|}{\sqrt{\frac{V_p}{3}}}$$

If the test statistic exceeds 2.13 then the supplier has failed to demonstrate a twenty percent difference between the high and low standards. In such a case, the standards are not acceptable.

2.2.5 The test statistic must be calculated:

Equation 6.

$$\text{TEST STATISTIC} = \frac{\left| M_2 - \frac{M_1}{1.8} - \frac{M_3}{2.2} \right|}{\sqrt{\frac{V_p}{4}}}$$

If the test statistic exceeds 2.13, the supplier has failed to demonstrate that the target standard concentration is midway between the high and low standards. In such a case, the standards are not acceptable.

2.2.6 The 95 percent confidence intervals for the mean result of each standard must be calculated:

Equation 7.

$$\text{Interval for Low Standard} = M_1 \pm (2.13)\sqrt{\frac{V_p}{6}}$$

Equation 8.

$$\text{Interval for Target Standard} = M_2 \pm (2.13)\sqrt{\frac{V_p}{6}}$$

Equation 9.

$$\text{Interval for High Standard} = M_3 \pm (2.13)\sqrt{\frac{V_p}{6}}$$

These intervals must not overlap. If overlap is observed, then the supplier has failed to demonstrate the ability to discriminate the 10 percent difference in concentrations. In such a case, the standards are not acceptable.

In any event, the Laboratory is responsible for the quality of the standards employed for analyses under this Protocol.

Section 3. -- Requesting Standards From the EPA Standards Repository

Solutions of analytical reference materials can be ordered from the U.S. EPA Chemical Standards Repository, depending on availability. The Laboratory can place an order for standards only after demonstrating that these standards are not available from commercial vendors either in solution or as a neat material.

Section 4. -- Documentation of the Verification and Preparation of Chemical Standards

It is the responsibility of each laboratory to maintain the necessary documentation to show that the chemical standards they have used in the performance of ASP analysis conform to the requirements previously listed. Weighing logbooks, calculations, chromatograms, mass spectra, etc., whether produced by the Laboratory or purchased from chemical supply houses, must be maintained by the Laboratory and may be subject to review during On-Site inspection visits. In those cases where the documentation is supportive of the analytical results of data packages sent to NYSDEC, such documentation is to be kept on file by the Laboratory for a period of one year.

Upon request by the Bureau of Watershed Assessment and Research or the Project Officer, the Laboratory shall submit their most recent previous year's documentation (12 months) for the verification and preparation of chemical standards within 14 days of the receipt of request to the recipients he/she designates.

The NYSDEC may generate a report discussing deficiencies in the Laboratory's documentation for the verification and preparation of chemical standards or may discuss the deficiencies during an On-Site laboratory evaluation. In a detailed letter to the Bureau of Watershed Assessment and Research or the Project Officer, the Laboratory shall address the deficiencies and the subsequent corrective action implemented by the Laboratory to correct the deficiencies within 14 days of receipt of the report or the On-Site laboratory evaluation.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Laboratory, the Laboratory shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section III.

If the Laboratory fails to adhere to the requirements listed in Section V, a Laboratory may expect, but the NYSDEC is not limited to the following actions: reduction of number of samples sent under the contract, suspension of sample shipment to the

Laboratory, GC/MS tape audit, data package audit, an On-Site laboratory evaluation, a remedial laboratory evaluation sample, and/or contract sanctions.

Part XIII -- Contract Compliance Screening

Contract Compliance Screening (CCS) is one aspect of the NYSDEC's contractual right of inspection of analytical data. CCS examines the Laboratory's adherence to the Protocol requirements based on the sample data package delivered to the NYSDEC.

CCS is performed by the Bureau of Watershed Assessment and Research or the Project Officer. To assure a uniform review, a set of standardized procedures has been developed to evaluate the sample data package submitted by a Laboratory against the technical and completeness requirements of the Protocol.

CCS results are mailed to the Laboratory and all other data recipients. The Laboratory has a period of time to correct deficiencies. The Laboratory must send all corrections to the Bureau of Program Services and Research or the Project Officer.

CCS results are used in conjunction with other information to measure overall Laboratory performance and to take appropriate actions to correct deficiencies in performance.

The NYSDEC may generate a CCS trend report which summarizes CCS results over a given period of time. The NYSDEC may send the CCS trend report or discuss the CCS trend report during an On-Site laboratory evaluation. In a detailed letter to the Bureau of Watershed Assessment and Research or the Project Officer, the Laboratory shall address the deficiencies and the subsequent corrective action implemented by the Laboratory to correct the deficiencies within 14 days of receipt of the report or the On-Site laboratory evaluation.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Laboratory, the Laboratory shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section III.

If the Laboratory fails to adhere to the requirements listed in Section VI, the Laboratory may expect, but the NYSDEC is not limited to the following actions: reduction of number of samples sent under the contract, suspension of sample shipment to the Laboratory, GC/MS tape audit, data package audit, an On-Site laboratory evaluation, a remedial laboratory evaluation sample, and/or contract sanctions.

Part XIV -- Program/Regional Office Data Review

Laboratory data are generated to meet the specific needs of the Programs and/or the Regions. In order to verify the usability of data for the intended purpose, each Program/Region reviews data from the perspective of end-user, based upon functional aspects of data quality. General guidelines for data review have been developed jointly by the Region and the Central Program Office. Each Program/Region uses these guidelines as the basis for data evaluation. Individual Programs/Regions may augment the basic guideline review process with additional review based on Program/Region-specific or site-specific concerns. Program/Regional reviews, like the sites under investigation, vary based on the nature of the problems under investigation and the Program/Regional response appropriate to the specific circumstances.

Program/Regional data reviews, relating usability of the data to a specific site, are part of the collective assessment process. They complement the review done at the Bureau of Wareshed Assessment and Research, which is designed to identify contractual discrepancies and to evaluate Laboratory and method performance. These individual evaluations are integrated into a collective review that is necessary for program and laboratory administration and management and may be used to take appropriate action to correct deficiencies in the Laboratory's performance.

Part XV -- Laboratory Evaluation Samples

Although intralaboratory QC may demonstrate Laboratory and method performance that can be tracked over time, an external performance evaluation program is an essential feature of a QA program. As a means of measuring Laboratory and method performance, Laboratories participate in interlaboratory comparison studies conducted by the NYSDEC. Results from the analysis of these laboratory evaluation samples, also referred to as performance evaluation (PE) samples, will be used by the NYSDEC to verify the Laboratory's continuing ability to produce acceptable analytical data. The results are also used to assess the precision and accuracy of the analytical methods for specific analytes.

Sample sets may be provided to participating Laboratories as frequently as on an SDG-by-SDG basis as a recognizable QC sample of known composition; as a recognizable QC sample of unknown composition; or not recognizable as a QC material. The laboratory evaluation samples may be sent either by the Program/Regional Office or the Bureau of Watershed Assessment and Research, and may be used for contract action.

Laboratories are required to analyze the samples and return the data package and all raw data within the Protocol required turnaround time.

At a minimum, the results are evaluated for compound identification, quantification, and sample contamination. Confidence intervals for the quantification of target compounds are based on reported values using population statistics. NYSDEC may adjust the scores on any given laboratory evaluation sample to compensate for unanticipated difficulties with a particular sample. Normally, a fraction of the compounds spiked into the sample are not specifically listed in the Protocol. Laboratories are required to use the NIST/EPA/MSDC mass spectral library to tentatively identify a maximum number of non-target compounds in each fraction that are present above a minimal response. Tentative identification of these compounds, based on Protocol described spectral interpretation procedures, is evaluated and integrated into the evaluation process.

A Laboratory's results on the laboratory evaluation samples will determine the Laboratory's performance as follows:

1. Acceptable, No Response Required (Score greater than or equal to 90 percent):

Data meets most or all of the scoring criteria. No response is required.

2. Acceptable, Response Explaining Deficiency(ies) Required (Score greater than or equal to 75 percent but less than 90 percent):

Deficiencies exist in the Laboratory's performance.

Within 14 days of receipt of notification from NYSDEC, the Laboratory shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the Bureau of Watershed Assessment and Research or the Project Officer.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by

the Laboratory, the Laboratory shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section III.

3. Unacceptable Performance, Response Explaining Deficiency(ies) Required (Score less than 75 percent):

Deficiencies exist in the Laboratory's performance to the extent that the Bureau of Watershed Assessment and Research or the Project Officer has determined that the Laboratory has not demonstrated the capability to meet the Protocol requirements.

Within 14 days of receipt of notification from NYSDEC, the Laboratory shall describe the deficiency(ies) and the action(s) taken to correct the deficiency(ies) in a letter to the Bureau of Watershed Assessment and Research or the Project Officer.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Laboratory, the Laboratory shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section III.

The Laboratory shall be notified by the Bureau of Watershed Assessment and Research or the Project Officer concerning the remedy for their unacceptable performance. A Laboratory may expect, but the NYSDEC is not limited to, the following actions: reduction of the number of samples sent under the contract, suspension of sample shipment to the Laboratory, an On-Site laboratory evaluation, GC/MS tape audit, data package audit, remedial laboratory evaluation sample, and/or a contract sanction.

***Note**: A Laboratory's prompt response demonstrating that corrective actions have been taken to ensure the Laboratory's capability to meet Protocol requirements may facilitate continuation of full sample delivery.*

If the Laboratory fails to adhere to the requirements listed in Section VIII, a Laboratory may expect, but the NYSDEC is not limited to the following actions: reduction in the number of samples sent under the Protocol, suspension of sample shipment to the Laboratory, an On-Site Laboratory Evaluation, GC/MS tape audit, data package audit, a remedial laboratory evaluation sample and/or contract sanctions.

Part XVI -- GC/MS Tape Audits

Periodically, NYSDEC may request from the Laboratory the GC/MS magnetic tapes corresponding to a specific case in order to accomplish tape audits. Generally, tape submissions and audits are requested for the following reasons:

- Program overview
- Indication of data quality problems from BPSR, or Program/Regional data reviews
- Support for On-Site audits
- Specific Regional requests

Depending upon the reason for an audit, the tapes from a recent case, a specific case, or a laboratory evaluation sample may be requested. Tape audits provide a mechanism to assess adherence to Protocol requirements and to ensure the consistency of data reported on the hardcopy/floppy diskettes with that generated on the GC/MS tapes. This function provides external monitoring of Program QC requirements and checks adherence of the Laboratory to internal QA procedures. In addition, tape audits enable NYSDEC to evaluate the utility, precision, and accuracy of the analytical methods.

The Laboratory must store all raw and processed GC/MS data on magnetic tape, in appropriate instrument manufacturer's format. This tape must include data for samples, blanks, matrix spikes, matrix spike duplicates, matrix spike blanks, QC Check Samples initial calibrations, continuing calibrations, BFB and DFTPP, as well as all laboratory-generated spectral libraries and quantitation reports required to generate the data package. The Laboratory shall maintain a written reference logbook of tape files to NYSDEC sample number, calibration data, standards, blanks, matrix spikes, matrix spike duplicates and matrix spike blanks. The logbook should include NYSDEC sample numbers and standard and blank ID's, identified by Case and Sample Delivery Group.

The Laboratory is required to retain the GC/MS tapes for 365 days after data submission.

When submitting GC/MS tapes to the NYSDEC, the following materials must be delivered in response to the request:

1. All associated raw data files for samples, blanks, matrix spikes, matrix spike duplicates, initial and continuing calibration standards, and instrument performance check solutions (BFB and DFTPP).

2. All processed data files and quantitation output files associated with the raw data files described above.

3. All associated identifications and calculation files used to generate the data submitted in the data package.

4. All laboratory-generated mass spectral library files (NIST/EPA/MSDC library not required).

5. A copy of the Laboratory's written reference logbook relating tape files to NYSDEC Sample Number, calibration data, standards, blanks, matrix spikes, matrix spike duplicates and matrix spike blanks. The logbook must include NYSDEC Sample Numbers and Lab File identifiers for all samples, blanks, and standards, identified by Case and SDG.

The Laboratory must also provide a statement attesting to the completeness of the GC/MS data tape submission, signed and dated by the Laboratory Manager. This statement must be part of a cover sheet that includes the following information relevant to the data tape submission:

1. Laboratory name
2. Date of submission
3. Case Number
4. SDG Number
5. GC/MS make and model number
6. Software version
7. Disk drive type (e.g. CDC, PRIAM, etc.)
8. File transfer method (e.g. DSD, DTD, FTP, Aquarius, etc.)
9. Names and telephone numbers of two laboratory contacts for further information regarding the submission.

Submission of the GC/MS tape:

Upon request of the Bureau of Watershed Assessment and Research or the Project Officer, the Laboratory shall send the required GC/MS tapes and all necessary documentation to the Bureau of Watershed Assessment and Research or the Project Officer within seven days of notification.

Responding to the GC/MS tape audit report:

After completion of the GC/MS tape audit, the NYSDEC may send a copy of the GC/MS tape audit report to the Laboratory or may discuss the GC/MS tape audit report on an On-Site laboratory evaluation. In a detailed letter to the Bureau of Watershed Assessment and Research or the Project Officer, the Laboratory shall discuss the corrective actions implemented to resolve the deficiencies listed in the GC/MS tape audit report within 14 days of receipt of the report.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Laboratory, the Laboratory shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section III.

Corrective actions

If the Laboratory fails to adhere to the requirements listed in Section IX, the Laboratory may expect, but the NYSDEC is not limited to the following actions: reduction in the number of samples sent under the contract, suspension of sample shipment to the Laboratory, an On-Site laboratory evaluation, GC/MS tape audit, data package audit, remedial laboratory evaluation sample, and/or contract sanctions.

Part XVI -- Data Package Audits

Data package audits are performed by the NYSDEC for program overview and specific Regional concerns. Standardized procedures have been established to assure uniformity of the auditing process. Data packages are periodically selected from recently received cases. They are evaluated for the technical quality of hardcopy raw data, quality assurance, and the adherence to contractual requirements. This function provides external monitoring of program QC requirements.

Data package audits are used to assess the technical quality of the data and evaluate overall laboratory performance. It provides the NYSDEC with an in-depth inspection and evaluation of the Case data package with regard to achieving QA/QC acceptability. A thorough review of the raw data is completed including: a check of instrument printouts, quantitations reports, chromatograms, spectra, library searches and other documentation for deviations from the contractual requirements, a check for transcription and calculation errors, a review of the qualifications of the laboratory personnel involved with the Case, and a review of all current SOPs on file.

Responding to the data package audit report:

After completion of the data package audit, the NYSDEC may send a copy of the data package audit report to the Laboratory or may discuss the data package audit report on an On-Site laboratory evaluation. In a detailed letter to the Bureau of Watershed Assessment and Research or the Project Officer, the Laboratory shall discuss the corrective actions implemented to resolve the deficiencies listed in the data package audit report within 14 days of receipt of the report.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Laboratory, the Laboratory shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section III.

Corrective Actions

If the Laboratory fails to adhere to the requirements listed in Section X, the Laboratory may expect, but the NYSDEC is not limited to the following actions: reduction in the numbers of samples sent under the contract, suspension of sample shipment to the Laboratory, an On-Site laboratory evaluation, GC/MS tape audit, data package audit, remedial laboratory evaluation sample, and/or contract sanctions.

Part XVII -- On-Site Laboratory Evaluations

At a frequency dictated by a Laboratory's performance, the Bureau of Watershed Assessment and Research or the Project Officer or their authorized representative will conduct an On-Site laboratory evaluation. On-site laboratory evaluations are carried out to monitor the Laboratory's ability to meet selected terms and conditions specified in the Protocol. The evaluation process incorporates two separate categories: Quality Assurance Evaluation, and an Evidentiary Audit.

Section 1. -- Quality Assurance On-Site Evaluation

1.1 Quality assurance evaluators inspect the Laboratory's facilities to verify the adequacy and maintenance of instrumentation, the continuity of personnel meeting experience or education requirements, and the acceptable performance of analytical and QC procedures. The Laboratory should expect that items to be monitored will include, but not be limited to the following items.

1.1.1 Size and appearance of the facility

1.1.2 Quantity, age, availability, scheduled maintenance and performance of instrumentation

1.1.3 Availability, appropriateness, and utilization of the QAPP and SOPs

1.1.4 Staff qualifications, experience, and personnel training programs

1.1.5 Reagents, standards, and sample storage facilities

1.1.6 Standard preparation logbooks and raw data

1.1.7 Bench sheets and analytical logbook maintenance and review

1.1.8 Review of the Laboratory's sample analysis/data package inspection/data management procedures

Prior to an On-Site evaluation, various documentation pertaining to performance of the specific Laboratory is integrated in a profile package for discussion during the evaluation. Items that may be included are previous On-Site reports, laboratory evaluation sample scores, Program/Regional review of data, Regional QA materials, GC/MS tape audit reports, data audit reports, results of CCS, and date trend reports.

Section 2. -- Evidentiary Audit

Evidence auditors conduct an On-Site laboratory evaluation to determine if laboratory policies and procedures are in place to satisfy evidence handling requirements as stated in Exhibit F. The evidence audit is comprised of the following three activities:

2.1 Procedural Audit

The procedural audit consists of review and examination of actual standard operating procedures and accompanying documentation for the following laboratory operations: sample receiving, sample storage, sample identification, sample security, sample

tracking (from receipt to completion of analysis) and analytical project file organization and assembly.

2.2 Written SOPs Audit

The written SOPs audit consists of review and examination of the written SOPs to determine if they are accurate and complete for the following laboratory operations: sample receiving, sample storage, sample identification, sample security, sample tracking (from receipt to completion of analysis) and analytical project file organization and assembly.

2.3 Analytical Project File Evidence Audit

The analytical project file evidence audit consists of review and examination of the analytical project file documentation. The auditors review the files to determine:

2.3.1 The accuracy of the document inventory

2.3.2 The completeness of the file

2.3.3 The adequacy and accuracy of the document numbering system

2.3.4 Traceability of sample activity

2.3.5 Identification of activity recorded on the documents

2.3.6 Error correction methods

Section 3. -- Discussion of the On-Site Team's Findings

The quality assurance and evidentiary auditors discuss their findings with the Bureau of Watershed Assessment and Research or the Project Officer prior to debriefing the Laboratory. During the debriefing, the auditors present their findings and recommendations for corrective actions necessary to the Laboratory personnel.

Section 4. -- Corrective Action Reports For Follow-Through to Quality Assurance and Evidentiary Audit Reports

On-site laboratory evaluation:

Following an On-Site laboratory evaluation, quality assurance and/or evidentiary audit reports which discuss deficiencies found during the On-Site evaluation may be sent to the Laboratory. In a detailed letter, the Laboratory shall discuss the corrective actions implemented to resolve the deficiencies discussed during the On-Site evaluation and discussed in the report(s) to the Bureau of Watershed Assessment and Research or the Project Officer (response to quality assurance/technical report and response to the evidentiary report), within 14 days of receipt of the report.

If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Laboratory,

the Laboratory shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section III.

Corrective actions

If the Laboratory fails to adhere to the requirements listed in Section XI, the Laboratory may expect, but the NYSDEC is not limited to the following actions: reduction in the number of samples sent under the contract, suspension of sample shipment to the Laboratory, an On-Site laboratory evaluation, GC/MS tape audit, data package audit, a remedial laboratory evaluation sample, and/or contract sanctions.

Part XVIII -- Quality Assurance And Data Trend Analysis

Data submitted by Laboratories are subject to review from several aspects: compliance with Protocol-required QC, usability, and full data package evaluation. Problems resulting from any of these reviews may determine the need for a GC/MS tape audit, an On-Site laboratory evaluation and/or a remedial laboratory evaluation sample. In addition, QC prescribed in the methods provides information that is continually used by the NYSDEC to assess sample data quality, Laboratory data quality and Program data quality via data trend analysis. Trend analysis is accomplished by entering data into a computerized data base. Statistical reports that evaluate specific anomalies or disclose trends in many areas, including the following, are generated from this data base:

- Surrogate Spike Recovery
- Laboratory Evaluation Sample
- Blanks
- GC/MS Instrument Performance Checks (BFB and DFTPP)
- Initial and Continuing Calibration Data
- Other QC and Method Parameters

Program-wide statistical results are used to rank laboratories in order to observe the relative performance of each Laboratory using a given Protocol against its peers. The reports are also used to identify trends within laboratories. The results of many of these trend analyses are included in overall evaluation of a Laboratory's performance, and are reviewed to determine if corrective action or an On-Site laboratory evaluation is indicated in order to meet the QA/QC requirements of the Protocol.

Laboratory performance over time is monitored using these trend analysis techniques to detect departures of Laboratory output from required or desired levels of quality control, and to provide an early warning of Laboratory QA/QC problems which may not be apparent from the results of an individual case.

As a further benefit to the Program, the data base provides the information needed to establish performance-based criteria in updated analytical protocols, where advisory criteria has been previously used. The vast empirical data set produced by Laboratories is carefully analyzed, with the results augmenting theoretical and research-based performance criteria.

The result is a continuously monitored set of quality control and performance criteria specifications of what is routinely achievable and expected of environmental chemistry laboratories in mass production analysis of environmental samples. This, in turn, assists the NYSDEC in meeting its objectives of obtaining data of known and documented quality.

Part XIX -- Data Management

Data management procedures are defined as procedures specifying the acquisition or entry, update, correction, deletion, storage and security of computer readable data and files. These procedures should be in written form and contain a clear definition for all databases and files used to generate or resubmit deliverables. Key areas of concern include: system organization (including personnel and security), documentation operations, traceability and quality control.

Data manually entered from hard-copy must be quality controlled and the error rates estimated. Systems should prevent entry of incorrect or out-of-range data and alert data entry personnel of errors. In addition, data entry error rates must be estimated and recorded on a monthly basis by reentering a statistical sample of the data entered and calculating discrepancy rates by data element.

The record of changes in the form of corrections and updates to data originally generated, submitted, and/or resubmitted must be documented to allow traceablilty of updates. Documentation must include the following for each change:

- Justification or rationale for the change.
- Initials of the person making the change or changes. Data changes must be implemented and reviewed by a person or group independent of the source generating the deliverable.
- Change documentation must be retained according to the schedule of the original deliverable.
- Resubmitted diskettes or other deliverables must be reinspected as a part of the Laboratories' internal inspection process prior to resubmission. The entire deliverable, not just the changes, must be inspected.
- The Laboratory Manager must approve changes to originally submitted deliverables.
- Documentation of data changes may be requested by laboratory auditors.

Lifecycle management procedures must be applied to compute software systems developed by the laboratory to be used to generate and edit contract deliverables. Such systems must be thoroughly tested and documented prior to utilization.

- A software test and acceptance plan including test requirements, test results and acceptance criteria must be developed, followed, and available in written form.
- System changes must not be made directly to production systems generating deliverables. Changes must be made first to a development system and tested prior to implementation.
- Each version of the production system will be given an identification number, date of installation, date of last operation and archived.

- System and operations documentation must be developed and maintained for each system. Documentation must include a users manual and an operations and maintenance manual.

Individual(s) responsible for the following functions must be identified:

- System operation and maintenance including documentation and training.
- Database integrity, including data entry, data updating and quality control.
- Data and system security, backup and archiving.

Part XX -- Laboratory Evaluation Procedures

This document outlines the procedures which will be used by the NYSDEC to conduct laboratory audits to determine the Laboratory's ability to meet the terms and conditions of this Protocol. The evaluation process incorporates two major steps: 1) evaluation of laboratory performance, and 2) on-site inspection of the laboratory to verify continuity of personnel, instrumentation and quality control requirements contained in the Protocol. The following is a description of these two steps.

Section 1 -- Evaluation of Laboratory Performance

1. Performance Evaluation Sample Analysis

1.1 The Performance Evaluation (PE) sample set will be sent to a participating laboratory on a semi-annual basis to verify the Laboratory's continuing ability to produce acceptable analytical results. These samples will be provided either single blind (recognizable as a PE material and of unknown composition), or double blind (not recognizable as a PE material and of unknown composition). If received as a single blind, the Laboratory is required to submit PE sample data in a separate SDG package in accordance with Delivery Schedule requirements for PE Sample data. PE samples received as double blind would be treated as routine samples and data would be submitted in the SDG deliverables package per normal procedure.

1.2 When the PE data are received, results will be scored routinely for identification and quantitation, according to the elements and weighting factors shown in the attached scoring sheets. Results of these scorings will be provided for the laboratory via coded evaluation spread sheets by compound classes. The NYSDEC may adjust the scores on any given PE sample to compensate for unanticipated difficulties with a particular sample.

1.3 If the Laboratory performs unacceptably, the Laboratory will be notified by the Bureau of Watershed Assessment and Research. A laboratory so notified may expect, but the NYSDEC is not limited to, the following actions: (1) a site visit, (2) a full data audit, (3) cessation of sample shipments, (4) and/or laboratory analysis of a second PE sample. Failure by the laboratory to take corrective actions and/or failure of two successive PE sample analyses is indicative of laboratory failure to maintain technical competence and will require that the laboratory discontinue analysis of samples until such time as BWAR has determined that the Laboratory has corrected the problem and may resume analyses.

1.4 Timeliness in delivering PE sample data to the NYSDEC is essential and is reflected in the deduction of points from the gross score for late data submissions. Late is defined as 31 days or more from the documented day of sample receipt.

B. Data Audit

Data audits are conducted by BWAR on the Laboratory's sample data packages. The data audit provides the NYSDEC with an in-depth inspection and evaluation of the data packages with regard to achieving QA/QC acceptability.

Part XXI -- Performance Sample Review Scoring Package

PERFORMANCE EVALUATION SAMPLE
REVIEW SCORING PACKAGE

Laboratory _____

Date _____

Sample # _____

Reviewer_____

PERFORMANCE EVALUATION SAMPLE VOLATILE ORGANICS RESULTS

The Performance Evaluation includes the analysis of one or more Performance Evaluation Samples supplied to the Laboratory by the NYSDEC. Each sample, and each scoring Category of each sample, is evaluated separately, according to the following scoring scheme. Each scoring Category of each sample analyzed by the Laboratory must receive a passing score in order for the Laboratory to pass the Performance Evaluation.

Sample ID: _____ **Matrix: _____**

I. IDENTIFICATION (200 points)

(Minimum passing score 150)

Total number of Category I points deducted _____

Points awarded for Category I _____

II. QUANTIFICATION (200 points)

(Minimum passing score 150)

Total number of Category II points deducted _____

Points awarded for Category II _____

III. QUALITY CONTROL (200 points)

(Minimum passing score 150)

Total number of Category III points deducted _____

Points awarded for Category III _____

IV. REPORTING AND DELIVERABLES (200 points)

(Minimum passing score 150)

Total number of Category IV points deducted _____

Points awarded for Category IV _____

The following variables are used in the calculation of the preliminary score, which includes the identification and quantification sections:

X = Number of target compounds included in the study, including those analytes with no acceptance windows

A = Number of target compounds in the study that were not identified

B = Number of target compounds misquantified

C = Number of target compound contaminants (i.e., target compounds not included in the study but identified by the Laboratory)

D = Number of tentatively identified compounds not identified

E = Number of tentatively identified compound contaminants (i.e., non-target compounds not included in the study but identified by the Laboratory)

I. IDENTIFICATION (200 points)

A. Target Compound Identifications (120 points)

$$\frac{(A)\ (1200)}{X} = \_\_\_\_\_ \text{ points deducted}$$

B. Target Compound Contaminants (50 points)

(C) (50) = _____ points deducted

C. Tentatively Identified Compounds (30 points)

(D + E) (30) = _____ points deducted

Total Section I Score _____

Total Section I Score/200 = % Score _____

Pass Volatile Organics Section I Yes _____No _____

II. TARGET COMPOUND QUANTIFICATION (200 points)

$$\frac{(B)\ (1000)}{(X - A)} = \_\_\_\_\_ \text{ points deducted}$$

Total Section II Score _____

Total Section II Score/200 = % Score _____

Pass Volatile Organics Section II Yes _____No _____

III. QUALITY CONTROL (200 points)

A. Instrument Quality Control

1. Instrument Performance Check

   a. For failure to perform a BFB instrument performance check at the required frequency, deduct 200 points. (FATAL ERROR)

   b. For any BFB instrument performance check analyzed separately or added to reagent water, with any ion abundance ratios outside criteria, deduct 200 points. (FATAL ERROR)

III. A. 1. Points Deducted _____

2. Initial Calibration

   a. For failure to perform initial calibration at the required frequency for any fraction, deduct 200 points. (FATAL ERROR)

   b. For initial calibration data for VOA fraction if more than 2 volatile compounds fail to meet ASP-specified minimum RRF or maximum %RSD criteria, deduct 100 points for any initial calibration sequence of standards which does not meet the criteria. (FATAL ERROR)

III. A. 2. Points Deducted _____

3. Continuing Calibration

   a. For failure to perform continuing calibrations for any fraction at the required frequency, deduct 200 points per fraction. (FATAL ERROR)

   b. For continuing calibration data for VOA fraction, if more than 2 volatile compounds fail to meet ASP-specified minimum RRF or maximum %D criteria, deduct 200 points for each continuing calibration standard which does not meet the criteria. (FATAL ERROR)

III. A. 3. Points Deducted _____

III.A. Subtotal _____

B. Sample/Method Quality Control

1. Analysis within ASP specified holding times

   a. For failure to meet the holding time requirements for any sample, deduct 200 points per occurrence. (FATAL ERROR)

III. B. 1. Points Deducted _____

2. Method Blank Analyses (40 points maximum deduction)

   a. Failure to perform the method blank analysis for any of the fractions will result in the deduction of 40 points.

   b. If any (one or more) target compounds are detected in the method blank above the contract required quantitation limit (5x the CRQL for methylene chloride. acetone, and 2-butanone), deduct 20 points per occurrence.

III. B. 2. Points Deducted _____

3. Internal Standard and System Monitoring Compounds (40 points maximum deduction)

   a. Failure to add the internal standard or system monitoring compounds to any sample or blank will result in the deduction of 40 points.

   b. For failure to meet recovery criteria for any system monitoring compound in any sample or blank, deduct 20 points per occurrence.

III. B. 3. Points Deducted _____

4. Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank (20 points maximum deduction)

   a. Utilization of wrong spiking concentration in the sample will result in deduction of 20 points.

   b. Failure to perform matrix spike, Matrix spike duplicate or matrix spike blank analysis will result in deduction of 20 points.

   c. Failure to meet matrix spike blank recovery criteria listed in Exhibit D, Part III, Table 8, deduct 20 points.

III. B. 4. Points Deducted _____

III.B. Subtotal _____ Total Section III Score _____

Total Section III Score/200 = % Score _____

Pass Volatile Organics Section III Yes _____No _____

IV. REPORTING AND DELIVERABLES (200 points)

A. BFB (50 points maximum deduction).

Mass listing and bar graph output must be submitted for each instrument and for every 12-hour period during which samples were analyzed. Deduct 25 points per violation.

IV. A. Points Deducted _____

B. RICs and quantitation reports (50 points maximum deduction).

Deduct 10 points for each of these required deliverables that are not submitted in accordance with the Analytical Services Protocol.

IV. B. Points Deducted _____

C. Mass spectra (50 points maximum deduction)

Deduct 10 points for each of the required deliverables in VOA fraction that are not submitted in accordance with the Analytical Services Protocol.

IV. C. Points Deducted _____

D. Contractual Forms for VOA fraction (50 points maximum deduction)

Deduct 50 points if any of the required ASP forms are not submitted in accordance with the Analytical Services Protocol.

IV. D. Points Deducted _____

Total Section IV Score _____

Total Section IV Score/200 = % Score _____

Pass Volatile Organics Section IV Yes _____No _____

PERFORMANCE EVALUATION SAMPLE SEMIVOLATILE ORGANICS RESULTS

The Performance Evaluation includes the analysis of one or more Performance Evaluation Samples supplied to the Laboratory by the NYSDEC. Each sample, and each scoring Category of each sample, is evaluated separately, according to the following scoring scheme. Each scoring Category of each sample analyzed by the Laboratory must receive a passing score in order for the Laboratory to pass the Performance Evaluation.

Sample ID: _____ **Matrix: _____**

I. IDENTIFICATION (200 points)

(Minimum passing score 150)

Total number of Category I points deducted _____

Points awarded for Category I _____

II. QUANTIFICATION (200 points)

(Minimum passing score 150)

Total number of Category II points deducted _____

Points awarded for Category II _____

III. QUALITY CONTROL (200 points)

(Minimum passing score 150)

Total number of Category III points deducted _____

Points awarded for Category III _____

IV. REPORTING AND DELIVERABLES (200 points)

(Minimum passing score 150)

Total number of Category IV points deducted _____

Points awarded for Category IV _____

The following variables are used in the calculation of the preliminary score, which includes the identification and quantification sections:

X = Number of target compounds included in the study, including those analytes with no acceptance windows

A = Number of target compounds in the study that were not identified

B = Number of target compounds misquantified

C = Number of target compound contaminants (i.e., target compounds not included in the study but identified by the Laboratory)

D = Number of tentatively identified compounds not identified

E = Number of tentatively identified compound contaminants (i.e., non-target compounds not included in the study but identified by the Laboratory)

I. IDENTIFICATION (200 points)

A. Target Compound Identifications (120 points)

$$\frac{(A)\ (1200)}{X} = \_\_\_\_\_ \text{ points deducted}$$

B. Target Compound Contaminants (50 points)

(C) (50) = _____ points deducted

C. Tentatively Identified Compounds (30 points)

(D + E) (30) = _____ points deducted

Total Section I Score _____

Total Section I Score/200 = % Score _____

Pass Semivolatile Organics Section I Yes _____ No _____

II. TARGET COMPOUND QUANTIFICATION (200 points)

$$\frac{(B)\ (1000)}{(X - A)} = \_\_\_\_\_ \text{ points deducted}$$

Total Section II Score _____

Total Section II Score/200 = % Score _____

Pass Semivolatile Organics Section II Yes _____No _____

III. QUALITY CONTROL (200 points)

A. Instrument Quality Control

1. Instrument Performance Check

   a. For failure to perform a DFTPP instrument performance check at the required frequency, deduct 200 points. (FATAL ERROR)

   b. For any DFTPP instrument performance check analyzed separately or as part of the calibration standard, with any ion abundance ratios outside criteria, deduct 200 points. (FATAL ERROR)

III. A. 1. Points Deducted _____

2. Initial Calibration

   a. For failure to perform initial calibration at the required frequency for any fraction, deduct 200 points. (FATAL ERROR)

   b. For initial calibration data for semivolatile fraction if more than 4 semivolatile compounds fail to meet ASP-specified minimum RRF or maximum %RSD criteria, deduct 200 points for each initial calibration sequence of standards which does not meet the criteria. (FATAL ERROR)

III. A. 2. Points Deducted _____

3. Continuing Calibration

   a. For failure to perform continuing calibrations for any fraction at the required frequency, deduct 200 points per fraction. (FATAL ERROR)

   b. For continuing calibration data for semi fraction, if more than 4 semivolatile compounds fail to meet ASP-specified minimum RRF or maximum %D criteria, deduct 200 points for any continuing calibration standard which does not meet the criteria. (FATAL ERROR)

III. A. 3. Points Deducted _____

III.A. Subtotal _____

B. Sample/Method Quality Control

1. Analysis within ASP specified holding times

   a. For failure to meet the holding time requirements for any sample, deduct 200 points per occurrence. (FATAL ERROR)

III. B. 1. Points Deducted _____

2. Method Blank Analyses (40 points maximum deduction)

   a. Failure to perform the method blank analysis for any of the fractions will result in the deduction of 40 points.

   b. If any (one or more) target compounds are detected in the method blank above the contract required quantitation limit (5x the CRQL for phthalate esters), deduct 20 points per occurrence.

III. B. 2. Points Deducted _____

3. Internal Standard and Surrogate Compounds (40 points maximum deduction)

   a. Failure to add the internal standard or surrogate compounds to any sample or blank will result in the deduction of 40 points.

   b. For failure to meet surrogate recovery criteria listed in Exhibit D, Part III, Table 6, in any sample or blank, deduct 20 points per occurrence.

III. B. 3. Points Deducted _____

4. Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank (20 points maximum deduction)

   a. Utilization of wrong spiking concentration in the sample will result in deduction of 20 points.

   b. Failure to perform matrix spike, matrix spike duplicate or matrix spike blank analysis will result in deduction of 20 points.

   c. Failure to meet matrix spike blank recovery criteria listed in Exhibit D, Part III, Table 7, deduct 20 points.

III. B. 4. Points Deducted _____

III.B. Subtotal _____

Total Section III Score _____

Total Section III Score/200 = % Score _____

Pass Semivolatile Organics Section III Yes _____No _____

IV. REPORTING AND DELIVERABLES (200 points)

A. DFTPP (50 points maximum deduction).

Mass listing and bar graph output must be submitted for each instrument and for every 12-hour period during which samples were analyzed. Deduct 25 points for each violation.

IV. A. Points Deducted _____

B. RICs and quantitation reports (50 points maximum deduction).

Deduct 10 points for each of these required deliverables that are not submitted in accordance with the Analytical Services Protocol.

IV. B. Points Deducted _____

C. Mass spectra (50 points maximum deduction)

Deduct 10 points for each of the required deliverables in semivolatile fraction that are not submitted in accordance with the Analytical Services Protocol.

IV. C. Points Deducted _____

D. Contractual Forms for semivolatile fraction (50 points maximum deduction)

Deduct 50 points for each of the required ASP forms are not submitted in accordance with the Analytical Services Protocol.

IV. D. Points Deducted _____

Total Section IV Score _____

Total Section IV Score/200 = % Score _____

Pass Semivolatile Organics Section IV Yes _____No _____

PERFORMANCE EVALUATION SAMPLE PESTICIDE/AROCLOR RESULTS

The Performance Evaluation includes the analysis of one or more Performance Evaluation Samples supplied to the Laboratory by the NYSDEC. Each sample, and each scoring Category of each sample, is evaluated separately, according to the following scoring scheme. Each scoring Category of each sample analyzed by the Laboratory must receive a passing score in order for the Laboratory to pass the Performance Evaluation.

Sample ID: _____ **Matrix: _____**

I. IDENTIFICATION (200 points)

(Minimum passing score 150)

Total number of Category I points deducted _____

Points awarded for Category I _____

II. QUANTIFICATION (200 points)

(Minimum passing score 150)

Total number of Category II points deducted _____

Points awarded for Category II _____

III. QUALITY CONTROL (200 points)

(Minimum passing score 150)

Total number of Category III points deducted _____

Points awarded for Category III _____

IV. REPORTING AND DELIVERABLES (200 points)

(Minimum passing score 150)

Total number of Category IV points deducted _____

Points awarded for Category IV _____

The following variables are used in the calculation of the scores for Categories I and II, the identification and quantification sections:

X = Number of target compounds included in the study, including those analytes with no acceptance windows

A = Number of target compounds in the study that were not identified

B = Number of target compounds misquantified

C = Number of target compound contaminants (i.e., target compounds not included in the study but identified by the Laboratory)

I. IDENTIFICATION (200 points)

A. Target Compound Identifications (150 points)

$$\frac{(A)\ (1500)}{X} = \_\_\_\_\_ \text{ points deducted}$$

B. Target Compound Contaminants (50 points)

(C) (50) = _____ points deducted

Total Section I Score _____

Total Section I Score/200 = % Score _____

Pass Pesticides/Aroclors Section I Yes _____No _____

II. TARGET COMPOUND QUANTIFICATION (200 points)

$$\frac{(B)\ (1000)}{(X - A)} = \_\_\_\_\_ \text{ points deducted}$$

Total Section II Score _____

Total Section II Score /200 = % Score _____

Pass Pesticides/Aroclors Section II Yes _____No _____

III. QUALITY CONTROL (200 points)

A. Instrument Quality Control

1. Initial Calibration (requirements apply to both GC columns).

   a. For failure to perform an initial calibration, on either column, when required, deduct 200 points. (FATAL ERROR)
   Points deducted _____

   b. If the standards in the initial calibration sequence are not analyzed in the order given in the ASP, deduct 5 points.
   Points deducted _____

   c. If the resolution of any analytes in the resolution check mixture or the performance evaluation mixture (PEM) fail to meet the ASP-specified criteria (> or equal to 60% resolution for the resolution check standard, 100% resolution for the PEM), deduct 25 points per occurrence.
   Points deducted _____

   d. If the retention times of any analyte in the PEM falls outside retention time window calculated during the initial calibration, deduct 15 points per occurrence.
   Points deducted _____

   e. If the relative percent difference between the calculated amount and true amount of any analyte in the PEM exceeds 25.0 percent, deduct 15 points per occurrence.
   Points deducted _____

   f. If the breakdown of either DDT or Endrin exceeds 20.0 percent or the combined breakdown, as defined in the ASP, exceeds 30.0 percent, deduct 20 points.
   Points deducted _____

   g. If the %RSD of the calibration factors of any single component analyte or surrogate exceeds 20.0 percent or the %RSD of the surrogates exceeds 30%, deduct 20 points. Allowances may be made for up to two single component target compounds, but not surrogates, to have %RSDs exceeding 20%, but those compounds must have %RSD less than or equal to 30%.
   Points deducted _____

2. Continuing Calibration (requirements apply to both GC columns)

   a. For failure to perform a continuing calibration by analyzing the required standard(s) and instrument blanks before and after the sample data, deduct 200 points. (FATAL ERROR)

      Points deducted _____

   b. If the retention times of any analytes in the continuing calibration standards falls outside a retention time calculated during the initial calibration, deduct 10 points per occurrence.

      Points deducted _____

   c. If the relative percent difference between the calculated amount and true amount of any analyte in the PEM or Individual Standard mixtures used to demonstrate continuing calibration exceeds 25.0 percent, deduct 10 points per occurrence.

      Points deducted _____

   d. If the breakdown of either DDT or Endrin exceeds 20.0 percent, or the combined breakdown, as defined in the ASP, exceeds 30.0 percent, deduct 5 points.

      Points deducted _____

Total points deducted for Section A._____ Score for Section A._____

B. Sample/Method Quality Control

1. Analysis within ASP specified holding times

    a. For failure to meet the holding time requirements for any sample, deduct 200 points per occurrence. (FATAL ERROR)

    Points deducted _____

2. Surrogate Retention Time Shift (40 points maximum deduction)

    a. For failure to meet the retention time criteria for the surrogates in any sample, blank, or standard, deduct 10 points per occurrence.

    Points deducted _____

3. Method Blank Analyses (30 points maximum deduction)

    a. If any (one or more) of the Pesticide/Aroclor compounds are detected in a method blank at > CRQL, deduct 30 points.

    Points deducted _____

    b. For failure to perform method blank analyses on both columns, deduct 20 points.

    Points deducted _____

4. Gel Permeation Chromatography (10 points maximum deduction)

    a. For failure to perform gel permeation chromatography (GPC) on any soil sample, deduct 10 points.

    Points deducted _____

5. Matrix Spike/Matrix Spike Duplicate/Matrix Spike Blank (20 points)

The matrix spike percent recovery and matrix spike relative percent difference are for advisory purposes only The matrix spike blank recovery is mandatory.

a. Utilization of wrong spiking concentration in the sample (deduct of 20 points)

Points deducted _____

b. Failure to perform matrix spike or matrix spike duplicate or matrix spike blank analysis (deduct of 20 points)

Points deducted _____

c. Failure to meet mandatory matrix spike blank recovery criteria listed in Exhibit D, Part IV (deduct of 20 points)

Points deducted _____

Total points deducted for Section B._____ Score for Section B._____

Total Section III Score _____

Total Section III Score/200 = % Score _____

Pass Pesticides/Aroclors Section III Yes _____ No _____

IV. REPORTING AND DELIVERABLES (200 points)

1. Chromatograms and Quantitation reports (100 point maximum deduction)

For failure to submit chromatograms that meet the specifications of Exhibits D and E regarding, baseline, peak response and on-scale peaks, deduct 20 points per occurrence.

Points deducted _____

2. Contractual Forms for Pesticide/Aroclor fraction (100 points maximum deduction)

For each of the required deliverables forms not submitted in accordance with the Analytical Services Protocol, deduct 20 points.

Points deducted _____

Total points deducted for Section IV._____

Total Section IV Score._____

Total Section IV Score/200 = % Score _____

Pass Pesticides/Aroclors Section IV Yes _____ No _____

PERFORMANCE EVALUATION SAMPLE INORGANIC RESULTS

The Performance Evaluation includes the analysis of one or more Performance Evaluation Samples supplied to the Laboratory by the NYSDEC. Each sample for inorganic analysis is evaluated separately, according to the following scoring scheme. Each sample analyzed by the Laboratory must receive a passing score for each Category in order for the Laboratory to pass the Performance Evaluation.

Sample ID: _____ **Matrix: _____**

I. IDENTIFICATION (200 points)

(minimum passing score 150 points)

Total number of Category I points deducted _____

Points awarded for Category I _____

II. QUANTIFICATION (200 points)

(minimum passing score 150 points)

Total number of Category II points deducted _____

Points awarded for Category II _____

III. QUALITY CONTROL (200 points)

(minimum passing score 150 points)

Total number of Category III points deducted _____

Points awarded for Category III _____

IV. REPORTING AND DELIVERABLES (200 points)

(minimum passing score 150 points)

Total number of Category IV points deducted _____

Points awarded for Category IV _____

The following variables are used in the calculation of the preliminary score, which includes the identification and quantification sections:

X = Number of target compounds included in the study, including those analytes with no acceptance windows

A = Number of target compounds in the study that were not identified

B = Number of target compounds misquantified

C = Number of target compound contaminants (i.e., target compounds <u>not</u> included in the study but identified by the Laboratory)

I. IDENTIFICATION (200 points)

A. Target Compound Identifications (150 points)

$$\frac{(A)\ (1500)}{X} = \_\_\_\_\_ \text{ points deducted}$$

B. Target Compound Contaminants (50 points)

(C) (25) = _____ points deducted

Total Section I Score _____

Total Section I Score/200 = % Score _____

Pass Inorganic Section I Yes _____ No _____

II. TARGET COMPOUND QUANTIFICATION (200 points)

$$\frac{(B)\ (1000)}{(X - A)} = \_\_\_\_\_ \text{ points deducted}$$

Total Section II Score _____

Total Section II Score/200 = % Score _____

Pass Inorganic Section II Yes _____ No _____

III. QUALITY CONTROL (200 points)

A. Initial Calibration Verification

1. All initial calibration verifications within acceptance criteria - no points deducted

2. One-two outside of acceptance criteria - 30 points deducted

3. Three-four outside acceptance criteria - 60 points deducted

4. More than four outside acceptance criteria - 100 points deducted

5. Failure to perform initial calibration - 200 points deducted (FATAL ERROR)

Parameters outside criteria _____

Points deducted _____ Score _____

B. Continuing Calibration Verification

1. All initial calibration verifications within acceptance criteria - no points deducted

2. One-two outside of acceptance criteria - 30 points deducted

3. Three-four outside acceptance criteria - 60 points deducted

4. More than four outside acceptance criteria - 100 points deducted

5. Failure to perform initial calibration - 200 points deducted (FATAL ERROR)

Parameters outside criteria _____

Points deducted _____ Score _____

C. Preparation Blank Analysis (Maximum 15 points deducted)

1. All preparation blanks within ASP required limits - no points deducted.

2. One-two parameters present in preparation blanks above the contract required detection limits - 8 points deducted

3. More than two parameters present in preparation blanks above the contract required detection limits - 15 points deducted

Parameters outside criteria _____

Points deducted _____ Score _____

D. Matrix Spike Recovery (Maximum 10 points deducted)

1. Failure to perform matrix spike analysis - 10 points deducted.

2. Utilization of wrong matrix spike concentrations - 10 points deducted.

Points deducted _____ Score _____

E. Duplicate Precision Results (Maximum 10 points deducted)

1. Failure to perform duplicate analysis - 10 points deducted.

Points deducted _____ Score _____

F. Laboratory control Sample Results (Maximum 15 points deducted)

1. All LCS percent recovery results within acceptance criteria - no points deducted.

2. One-two LCS percent recovery results outside criteria - 8 points deducted.

3. Three-four LCS percent recovery results outside criteria - 12 points deducted

4. More than two LCS percent recovery results outside criteria - 15 points deducted.

Parameters outside criteria _____

Points deducted _____ Score _____

Total points deducted for Section III._____

Total Section III Score._____

Total Section III Score/200 = % Score _____

Pass Inorganic Section III Yes _____ No _____

IV. REPORTING AND DELIVERABLES (200 points)

Failure to submit any of the required deliverables in accordance with Exhibit B will result in deducting the following assigned points.

a. Raw instrument data for standards (20 points deducted per standard)

Points deducted _____

b. Raw instrument data for samples (20 points deducted per sample)

Points deducted _____

c. All ASP specified forms filled out correctly (20 points deducted per form)

Points deducted _____

Total points deducted for Section IV._____

Total Section IV Score._____

Total Section IV Score/200 = % Score _____

Pass Inorganic Section IV Yes _____ No _____

PERFORMANCE EVALUATION SAMPLE TCLP RESULTS

The Performance Evaluation includes the analysis of one or more Performance Evaluation Samples supplied to the Laboratory by the NYSDEC. Each sample for inorganic analysis is evaluated separately, according to the following scoring scheme. Each sample analyzed by the Laboratory must receive a passing score for each Category in order for the Laboratory to pass the Performance Evaluation.

Sample ID: _____ **Matrix: _____**

I. IDENTIFICATION (200 points)

(minimum passing score 150 points)

Total number of Category I points deducted _____

Points awarded for Category I _____

II. QUANTIFICATION (200 points)

(minimum passing score 150 points)

Total number of Category II points deducted _____

Points awarded for Category II _____

III. QUALITY CONTROL (200 points)

(minimum passing score 150 points)

Total number of Category III points deducted _____

Points awarded for Category III _____

IV. REPORTING AND DELIVERABLES (200 points)

(minimum passing score 150 points)

Total number of Category IV points deducted _____

Points awarded for Category IV _____

The following variables are used in the calculation of the preliminary score, which includes the identification and quantification sections:

X = Number of target compounds included in the study, including those analytes with no acceptance windows

A = Number of target compounds in the study that were not identified

B = Number of target compounds misquantified

C = Number of target compound contaminants (i.e., target compounds <u>not</u> included in the study but identified by the Laboratory)

I. IDENTIFICATION (200 points)

A. Target Compound Identifications (150 points)

$\frac{(A)\ (1500)}{X}$ = _____ points deducted

B. Target Compound Contaminants (50 points)

(C) (25) = _____ points deducted

Total Section I Score _____

Total Section I Score/200 = % Score _____

Pass TCLP Section I Yes _____ No _____

II. TARGET COMPOUND QUANTIFICATION (200 points)

$\frac{(B)\ (1000)}{(X - A)}$ = _____ points deducted

Total Section II Score _____

Total Section II Score/200 = % Score _____

Pass TCLP Section II Yes _____ No _____

III. QUALITY CONTROL (200 points)

A. Initial Calibration Verification

1. All initial calibration verifications within acceptance criteria - no points deducted

2. One or more volatile standards outside of acceptance criteria - 25 points deducted

3. One or more semivolatile standards outside acceptance criteria - 25 points deducted

4. One or more pesticide/herbicide standards outside acceptance criteria - 25 points deducted

5. One or more metals standards outside acceptance criteria - 25 points deducted

Parameters outside criteria _____

III. A. Points Deducted _____

B. Continuing Calibration Verification

1. All initial calibration verifications within acceptance criteria - no points deducted

2. One or more volatile standards outside of acceptance criteria - 25 points deducted

3. One or more semivolatile standards outside acceptance criteria - 25 points deducted

4. One or more pesticide/herbicide standards outside acceptance criteria - 25 points deducted

5. One or more metals standards outside acceptance criteria - 25 points deducted

Parameters outside criteria _____

III. B. Points Deducted _____

C. Preparation Blank Analysis (Maximum 20 points deducted)

1. All preparation blanks within ASP required limits - no points deducted.

2. One-two TCLP parameters present in preparation blanks above the contract required detection limits - 10 points deducted

3. More than two TCLP parameters present in preparation blanks above the contract required detection limits - 20 points deducted

4. Failure to perform Method Blank analysis- 20 points deducted

Parameters outside criteria _____

III. C. Points Deducted _____

D. Matrix Spike Recovery (Maximum 15 points deducted)

1. Failure to perform matrix spike analysis - 15 points deducted.

III. D. Points Deducted _____

E. Laboratory control Sample Results (Maximum 15 points deducted)

1. All LCS percent recovery results within acceptance criteria - no points deducted.

2. One-two LCS percent recovery results outside criteria - 8 points deducted.

3. Three-four LCS percent recovery results outside criteria - 12 points deducted

4. More than two LCS percent recovery results outside criteria - 15 points deducted.

Parameters outside criteria _____

III. E. Points Deducted _____

Total points deducted for Section III._____

Total Section III Score._____

Total Section III Score/200 = % Score _____

Pass TCLP Section III Yes _____ No _____

IV. REPORTING AND DELIVERABLES (200 points)

Failure to submit any of the required deliverables in accordance with Exhibit B will result in deducting the following assigned points.

A. Raw instrument data for inorganic standards (20 points deducted per standard)

Points deducted _____

B. Raw inorganic instrument data for samples (20 points deducted per sample)

Points deducted _____

C. Was the Method of Standard Additions used to determine the inorganic concentration (20 points deducted per sample)

Points deducted _____

D. Raw instrument data for volatile organics standards (20 points deducted per standard)

Points deducted _____

E. Raw volatile organics instrument data for samples (20 points deducted per sample)

Points deducted _____

F. Raw instrument data for semivolatile organics standards (20 points deducted per standard)

Points deducted _____

G. Raw semivolatile organics instrument data for samples (20 points deducted per sample)

Points deducted _____

H. Raw instrument data for pesticide/herbicide standards (20 points deducted per standard)

Points deducted _____

I. Raw pesticide/herbicide instrument data for samples (20 points deducted per sample)

Points deducted _____

Total Points deducted _____

Total Section IV Score _____

Total Section IV Score/200 = % Score _____

Pass TCLP Section IV Yes _____ No _____

Laboratory: _____ Sample ID: _____ Matrix: _____

SUMMARY

1. Volatile Organics Analysis

Section I	Pass	Yes _____	No _____
Section II	Pass	Yes _____	No _____
Section III	Pass	Yes _____	No _____
Section IV	Pass	Yes _____	No _____

2. Semivolatile Organics Analysis

Section I	Pass	Yes _____	No _____
Section II	Pass	Yes _____	No _____
Section III	Pass	Yes _____	No _____
Section IV	Pass	Yes _____	No _____

3. Pesticides/Aroclors Analysis

Section I	Pass	Yes _____	No _____
Section II	Pass	Yes _____	No _____
Section III	Pass	Yes _____	No _____
Section IV	Pass	Yes _____	No _____

4. Inorganics Analysis

Section I	Pass	Yes _____	No _____
Section II	Pass	Yes _____	No _____
Section III	Pass	Yes _____	No _____
Section IV	Pass	Yes _____	No _____

5. TCLP Analysis

Section I	Pass	Yes _____	No _____
Section II	Pass	Yes _____	No _____
Section III	Pass	Yes _____	No _____
Section IV	Pass	Yes _____	No _____

Overall PE Sample Study Pass Yes _____ No _____

EXHIBIT F

CHAIN-OF-CUSTODY, DOCUMENT CONTROL, AND STANDARD OPERATING PROCEDURES

1. Sample Chain-of-Custody

A sample is physical evidence collected from a facility or from the environment. Controlling evidence is an essential part of the hazardous waste investigation effort. To accomplish this, Laboratories are required to develop and implement the following sample identification, chain-of-custody, sample receiving, and sample tracking procedures.

1.1 Sample Identification

To assure traceability of the samples while in possession of the Laboratory, the Laboratory shall have a specified method for maintaining identification of samples throughout the Laboratory.

Each sample and sample preparation container shall be labeled with the NYSDEC number or a unique laboratory identifier. If a unique laboratory identifier is used, it shall be cross-referenced to the NYSDEC number.

1.2 Chain-of-Custody Procedures

Because of the nature of the data being collected, the custody of NYSDEC samples must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. The Laboratory shall have procedures ensuring that NYSDEC sample custody is maintained and documented. A sample is under custody if:

- It is in your possession, or
- It is in your view after being in your possession, or
- It was in your possession and you locked it up, or
- It is in a designated secure area. (Secure areas shall be accessible only to authorized personnel.)

1.3 Sample Receiving Procedures

1.3.1 The Laboratory shall designate a sample custodian responsible for receiving all samples.

1.3.2 The Laboratory shall designate a representative to receive samples in the event that the sample custodian is not available.

1.3.3 The condition of the shipping containers and sample bottles shall be inspected upon receipt by the sample custodian or his/her representative.

1.3.4 The condition of the custody seals (intact/not intact) shall be inspected upon receipt by the sample custodian or his/her representative.

1.3.5 The sample custodian or his/her representative shall check for the presence or absence of the following documents accompanying the sample shipment:

- o Airbills or airbill stickers
- o Custody seals
- o NYSDEC custody records
- o NYSDEC Contract Laboratory Sample Information sheets
- o Sample tags

1.3.6 The sample custodian or his/her representative shall sign and date all forms (e.g., custody records, or packing lists, and airbills) accompanying the samples at the time of sample receipt.

1.3.7 The Laboratory shall contact the Bureau of Program Services and Research or the Project Officer to resolve discrepancies and problems such as absent documents, conflicting information, broken custody seals, and unsatisfactory sample condition (e.g., leaking sample bottle).

1.3.8 The Laboratory shall record the resolution of discrepancies and problems on Telephone Contact Logs.

1.3.9 The following information shall be recorded on Form DC-1 (See Exhibit B) by the sample custodian or his/her representative as samples are received and inspected:

- o Condition of the shipping container
- o Presence or absence and condition of custody seals on shipping and/or sample containers
- o Custody seal numbers, when present
- o Condition of the sample bottles
- o Presence or absence of airbills or airbill stickers
- o Airbill or airbill sticker numbers
- o Presence or absence of custody records
- o Presence or absence of NYSDEC Contract Laboratory Sample Information Sheets
- o Presence or absence of sample tags
- o Sample tag identification numbers cross-referenced to the NYSDEC sample numbers

- o Verification of agreement or non-agreement of information recorded on shipping documents and sample containers

- o Problems or discrepancies

1.4 Sample Tracking Procedures

The Laboratory shall maintain records documenting all phases of sample handling from receipt to final analysis.

2. Document Control Procedures

The goal of the Laboratory document control program is to assure that all documents for a specified Sample Delivery Group (SDG) will be accounted for when the project is completed. Accountable documents used by Protocol laboratories shall include, but not be limited to, logbooks, chain-of-custody records, sample work sheets, bench sheets, and other documents relating to the sample or sample analyses. The following document control procedures have been established to assure that all laboratory records are assembled and stored for delivery to NYSDEC or are available upon request from NYSDEC prior to the delivery schedule.

2.1 Preprinted Laboratory Forms and Logbooks

2.1.1 All documents produced by the Laboratory which are directly related to the preparation and analysis of NYSDEC samples shall become the property of the NYSDEC and shall be placed in the complete sample delivery group file (CSF). All observations and results recorded by the Laboratory but not on preprinted laboratory forms shall be entered into permanent laboratory logbooks. When all data from a SDG is compiled, all original laboratory forms and copies of all SDG-related logbook entries shall be included in the documentation package.

2.1.2 The Laboratory shall identify the activity recorded on all laboratory documents which are directly related to the preparation and analysis of NYSDEC samples.

2.1.3 Pre-printed laboratory forms shall contain the name of the Laboratory and be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

2.1.4 Logbook entries shall be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

2.1.5 Logbook entries shall be in chronological order. Entries in logbooks, with the exception of instrument run logs and extraction logs, shall include only one SDG per page.

2.1.6 Pages in both bound and unbound logbooks shall be sequentially numbered.

2.1.7 Instrument run logs shall be maintained so as to enable a reconstruction of the run sequence of individual instruments. Because the Laboratory must provide copies of the instrument run logs to NYSDEC, the Laboratory may exercise the option of using only laboratory or NYSDEC sample identification numbers in the logs for sample ID rather than government agency or commercial client names to preserve the confidentiality of commercial clients.

2.1.8 Corrections to supporting documents and raw data shall be made by drawing a single line through the error and entering the correct information. Corrections and additions to supporting documents and raw data shall be dated and initialed. No information shall be obliterated or rendered unreadable.

All notations shall be recorded in ink.

Unused portions of documents shall be "z'd" out.

2.2 Consistency of Documentation

The Laboratory shall assign a document control officer responsible for the organization and assembly of the CSF.

All copies of laboratory documents shall be complete and legible.

Original documents which include information relating to more than one SDG shall be filed in the CSF of the lowest SDG number. The copy(s) shall be placed in the other CSF(s) and the Laboratory shall record the following information on the copy(s) in red ink:

"COPY

ORIGINAL IS FILED IN CSF _____"

The Laboratory shall sign and date this addition to the copy(s).

Before releasing analytical results, the document control officer shall assemble and cross-check the information on samples tags, custody records, lab bench sheets, personal and instrument logs, and other relevant deliverables to ensure that data pertaining to each particular sample or sample delivery group is consistent throughout the CSF.

2.3 Document Numbering and Inventory Procedure

In order to provide document accountability of the completed analysis records, each item in the CSF shall be inventoried and assigned a serialized number as described in Exhibit B).

All documents relevant to each sample delivery group, including logbook pages, bench sheets, mass spectra, chromatograms, screening records, re-preparation records, re-analysis records, records of failed or attempted analysis, custody records, library research results, etc. shall be inventoried.

The Document Control Officer (DCO) shall be responsible for ensuring that all documents generated are placed in the CSF for inventory and are delivered to the appropriate NYSDEC Office or other receiver as designated by NYSDEC. The DCO shall place the sample tags in plastic bags in the file.

2.4 Storage of NYSDEC Files

The Laboratory shall maintain NYSDEC laboratory documents in a secure location.

2.5 Shipment of Deliverables

The Laboratory shall document shipment of deliverables packages to the recipients. These shipments require custody seals on the containers placed such that they cannot be opened without damaging or breaking the seal. The Laboratory shall document what was sent, to whom, the date, and the method (carrier) used. A copy of the transmittal letter for the CSF shall be sent to the Bureau of Technical Services and Research.

3. Specifications for Written Standard Operating Procedures

The Laboratory shall have written standard operating procedures (SOPs) for receipt of samples, maintenance of custody, sample identification, sample storage, sample tracking, and assembly of completed data. An SOP is defined as a written narrative stepwise description of laboratory operating procedures including examples of laboratory documents. The SOPs shall accurately describe the actual procedures used in the Laboratory, and copies of the written SOPs shall be available to the appropriate laboratory personnel. These procedures are necessary to ensure that analytical data produced under this Protocol are acceptable for use in NYSDEC enforcement case preparation and litigation. The Laboratory's SOPs shall provide mechanisms and documentation to meet each of the following specifications and shall be used by NYSDEC as the basis for laboratory evidence audits.

3.1 The Laboratory shall have written SOPs describing the sample custodian's duties and responsibilities.

3.2 The Laboratory shall have written SOPs for receiving and logging in of the samples. The procedures shall include but not be limited to documenting the following information:

3.2.1 Presence or absence of NYSDEC chain-of-custody forms

3.2.2 Presence or absence of airbills or airbill stickers

3.2.3 Presence or absence of Contract Laboratory Sample Information Sheets

3.2.4 Presence or absence of custody seals on shipping and/or sample containers and their condition

3.2.5 Custody seal numbers, when present

3.2.6 Airbill or airbill sticker numbers

3.2.7 Presence or absence of sample tags

3.2.8 Sample tag ID numbers

3.2.9 Condition of the shipping container

3.2.10 Condition of the sample bottles

3.2.11 Verification of agreement or non-agreement of information on receiving documents and sample containers

3.2.12 Resolution of problems or discrepancies with the Bureau of Program Services and Research

3.2.13 An explanation of any terms used by the Laboratory to describe sample condition upon receipt (e.g., good, fine, OK)

3.3 The Laboratory shall have written SOPs for maintaining identification of NYSDEC samples throughout the Laboratory.

If the Laboratory assigns unique laboratory identifiers, written SOPs shall include a description of the method used to assign the unique laboratory identifier and shall include a description of the document used to cross-reference the unique laboratory identifier to the NYSDEC sample number.

If the Laboratory uses prefixes or suffixes in addition to sample identification numbers, the written SOPs shall include their definitions.

3.4 The Laboratory shall have written SOPs describing all storage areas for samples in the laboratory. The SOPs shall include a list of authorized personnel who have access or keys to secure storage areas.

3.5 The Laboratory shall have written SOPs describing the method by which the Laboratory maintains samples under custody.

3.6 The Laboratory shall have written SOPs describing the method by which the Laboratory maintains the security of any areas identified as secure.

3.7 The Laboratory shall have written SOPs for tracking the work performed on any particular samples. The tracking SOP shall include:

- o A description of the documents used to record sample receipt, sample storage, sample transfers, sample preparations, and sample analyses.
- o A description of the documents used to record calibration and QA/QC laboratory work.
- o Examples of document formats and laboratory documents used in the sample receipt, sample storage, sample transfer, and sample analyses.
- o A narrative step-wise description of how documents are used to track samples.

3.8 The Laboratory shall have written SOPs for organization and assembly of all documents relating to each SDG. Documents shall be filed on a sample delivery group-specific basis. The procedures shall ensure that all documents including logbook pages, sample tracking records, chromatographic charts, computer printouts, raw data summaries, correspondence, and any other written documents having reference to the SDG are compiled in one location for submission to NYSDEC. The written SOPs shall include:

- o A description of the numbering and inventory method.
- o A description of the method used by the Laboratory to verify consistency and completeness of the CSF.
- o Procedures for the shipment of deliverables packages using custody seals.

4. Handling of Confidential Information

A Laboratory conducting work under this Protocol may receive NYSDEC-designated confidential information from the agency. Confidential information must be handled separately from other documentation developed under this contract. To accomplish this, the following procedures for the handling of confidential information have been established.

4.1 All confidential documents shall be under the supervision of a designated document control officer (DCO).

4.2 Confidential Information

Any samples or information received with a request of confidentiality shall be handled as "confidential." A separate locked file shall be maintained to store this information and shall be segregated from other non-confidential information. Data generated from confidential samples shall be treated as confidential. Upon receipt of confidential information, the DCO will log these documents into a Confidential Inventory Log. The information will then be available to authorized personnel but only after it has been signed out to that person by the DCO. The documents shall be returned to the locked file at the conclusion of each working day. Confidential information may not be reproduced except upon approval by the Bureau of Program Services and Research or the Project Officer. The DCO will enter all copies into the document control system described above. In addition, this information may not be disposed of except upon approval by the Bureau of Program services and Research or the Project Officer. The DCO shall remove and retain the cover page of any confidential information disposed of for one year and shall keep a record on the disposition in the Confidential Inventory Log.

EXHIBIT G

GLOSSARY OF TERMS

GLOSSARY OF TERMS

ABSORBANCE - a measure of the decrease in incident light passing through a sample into the detector. It is defined mathematically as:

$$A = \frac{I\ (solvent)}{I\ (solution)} = \log \frac{I_o}{I}$$

Where; I = radiation intensity

ACCURACY - the closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

ALIQUOT - a measured portion of a field sample taken from analysis.

ANALYSIS DATE/TIME - the date and military time (24-hour clock) of the injection of the sample, standard, or blank into the analysis system.

ANALYTE - the element or ion an analysis seeks to determine; the element of interest.

ANALYTICAL SAMPLE - any solution or media introduced into an instrument on which an analysis is performed excluding instrument calibration, initial calibration verification, initial calibration blank, continuing calibration blank, and continuing calibration verification. Note the following are all defined as analytical samples: undiluted and diluted samples (NYSDEC and non-NYSDEC), predigestion spike samples, duplicate samples, serial dilution samples, analytical spike samples, post-digestion spike samples, interference check samples (ICS), CRDL standard for AA (CRA), CRDL standard for ICP (CRI), laboratory control sample (LCS), preparation blank (PB) and linear range analysis sample (LRS).

ANALYTICAL SERVICES PROTOCOL - the collection of analytical methods and corresponding reporting and quality control procedures that has been adopted by the New York State Department of Environmental Conservation.

ANALYTICAL SPIKE - the furnace post-digestion spike. The addition of a known amount of standard after digestion.

ASP - see Analytical Services Protocol

AUTOZERO - zeroing the instrument at the proper wavelength. It is equivalent to running a standard blank with the absorbance set at zero.

AVERAGE INTENSITY - the average of two different injections (exposures).

BACKGROUND CORRECTION - a technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

BAR GRAPH SPECTRUM - a plot of the mass-to-charge ratio (m/e) versus relative intensity of the ion current.

BATCH - a group of samples prepared at the same time in the same location using the same method, which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BIAS - the deviation due to matrix effects of the measured value (x_s - x_u) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (x_s - x_u) - K$$

where:

x_s = measured value for spiked sample,
x_u = measured value for unspiked sample, and
K = known value of the spike in the sample.

Using the following equations yields the percent recovery

$$\%R = 100 \left(\frac{x_s -- x_u}{K} \right)$$

BLANK - see specific type (e.g. Calibration Blank).

4-BROMOFLUOROBENZENE (BFB) - compound chosen to establish mass spectral tuning performance for volatile analyses.

BUREAU OF WATERSHED ASSESSMENT AND RESEARCH - the NYSDEC office responsible for contract laboratory coordination and compliance. Telephone number (518) 457-1630.

BWAR - see Bureau of Watershed Assessment and Research

CALIBRATION - the establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type or concentration of reagents as used in the sample preparation.

CALIBRATION BLANK - a volume of acidified deionized/distilled water.

CALIBRATION CHECK COMPOUNDS (CCC) - target compounds used to evaluate the calibration stability (precision) of the GC/MS system. Maximum percent deviations of the CCCs are defined in the protocol.

CASE - a finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Bureau of Technical Services and Research. A Case consists of one or more Sample Delivery Groups.

CHARACTERIZATION - a determination of the approximate concentration range of compounds of interest used to choose the appropriate analytical protocol.

CLP - refers to the United States Environmental Protection Agency's Contract Laboratory Protocol.

COEFFICIENT OF VARIATION (CV) - the standard deviation as a percent of the arithmetic mean.

CONCENTRATION LEVEL (Low or medium) -

For inorganic analysis, low or medium level is defined by the appropriate designation checked by the sample on the Contract Lab Sample Information Sheet.

For organic analysis, characterization of soil samples or sample fractions as low concentration of medium concentration is made on the basis of the Laboratory's preliminary screen, **not** on the basis of information entered on the Contract Lab Sample Information Sheet by the sampler.

CONFIRMATION ANALYSIS - see Primary Analysis.

CONTINUING CALIBRATION - analytical standard run at the Protocol specified periods to verify the calibration of the analytical system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

CONTRACT LAB SAMPLE INFORMATION SHEET - an NYSDEC sample identification form filled out by the sampler, which accompanies the sample during shipment to the Laboratory and which is used for documenting sample condition and receipt by the Laboratory, and analyses to be performed.

CONTRACT REQUIRED QUANTITATION LIMIT (CRQL) - minimum level of quantitation acceptable under the Protocol

CONTROL LIMITS - a range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that non-compliant data be flagged.

CONTROL SAMPLE - a QC sample Introduced Into a process to monitor the performance of the system.

CORRELATION COEFFICIENT - a number (r) which indicates the degree of dependence between two variables (concentration - absorbance). The more dependent they are the closer the value to one. Determined on the basis of the least squares line.

DATA COMPLETENESS - the percentage of requested analytical results for which valid results are reported.

DATA QUALITY OBJECTIYES (DQOs) - a statement of the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. This is qualitatively distinct from quality measurements such as precision, bias, and detection limit.

DAY - unless specified, day shall mean calendar day.

DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP) - compound chosen to establish mass spectral instrument performance for semivolatile analysis.

DIGESTION LOG - an official record of the sample preparation (digestion).

DISSOLVED METALS - analyte elements which have been passed through a 0.45 µm filter prior to preservation, digestion, or analysis.

DRY WEIGHT - the weight of a sample based on percent solids. The weight after drying in an oven.

DUPLICATE - a second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

EQUIPMENT RINSATE - a sample of analyte-free media which has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.

EXTRACTABLE - a compound that can be partitioned into an organic solvent from the sample matrix and is amenable to gas chromatography. Extractables include semivolatile (BNA) and pesticide/Aroclor compounds.

FIELD BLANK - any sample submitted to the Laboratory identified as a blank prepared in the field.

FIELD DUPLICATES - independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

FIELD SAMPLE - a portion of material received to be analyzed that is contained in single or multiple containers and identified by a unique NYSDEC Sample Number.

FLAME ATOMIC ABSORPTION (AA) - atomic absorption which utilizes flame for excitation.

GRAPHITE FURNACE ATOMIC ABSORPTION (GFAA) - atomic absorption which utilizes a graphite cell for excitation.

HOLDING BLANK - an aliquot of reagent water that is stored with environmental samples to demonstrate that the samples have not been contaminated during storage.

HOLDING TIME - the elapsed time expressed in days from the date of receipt of the sample by the Laboratory until the date of its preparation (digestion or distillation, or extraction) and/or analysis.

Holding time - (sample preparation date - sample receipt date)

ICP - see Inductively Coupled Plasma

INDEPENDENT STANDARD - a Laboratory-prepared standard solution that is composed of analytes from a different source than those used in the standards for the initial calibration.

INDUCTIVELY COUPLED PLASMA (ICP) - a technique for the simultaneous or sequential multi-element determination of elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Characteristic atomic line emission spectra are produced by excitation of the sample in a radio frequency inductively coupled plasma.

IN-HOUSE - at the Laboratory's facility.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the response of the analytical instrument to the target compounds.

INJECTION - introduction of the analytical sample into the instrument excitation system for the purpose of measuring absorbance, emission or concentration of an analyte. May also be referred to as exposure.

INSTRUMENT CALIBRATION - see INITIAL CALIBRATION

INSTRUMENT DETECTION LIMIT (IDL) -

For inorganics it is determined by multiplying by the Students t-Test value the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water) at a concentration of 3x-5x the estimated IDL on three days with a minimum of seven measurements per day.

For organics it is determined by multiplying by the Students t-Test value the standard deviation obtained for minimum of three replicate analyses of a standard solution at a concentration of 3x-5x the estimated IDL (each analyte in reagent water).

The standard deviation (s_c) at this concentration is then calculated with n-1 degrees of freedom. The instrument detection limits shall be calculated as follows:

$$IDL = t_{n-1} \times s_c$$

where t_{n-1} is the Students t-Test value for a 99% confidence level at the n-1 level and n is the number of replicates. For three replicates, t_{n-1} = 6.965 and for twenty-one replicates, t_{n-1} = 2.528.

INTERFERENTS - substances which affect the analysis for the element of interest.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix, spike, matrix spike duplicate, matrix spike blank, sample (for VOAs), and sample extract (for semivolatiles) at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds.

LABORATORY - synonymous with Contractor as used herein.

LABORATORY CONTROL SAMPLE (LCS) - a control sample of known composition spiked with compounds(s) representative of the target analytes. Aqueous and solid laboratory control samples are analyzed using the same sample preparation, reagents, and analytical methods employed for the NYSDEC samples received.

LABORATORY RECEIPT DATE - the date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and sample Chain-of-Custody. Also referred to as VTSR (Validated time of sample receipt).

LINEAR RANGE, LINEAR DYNAMIC RANGE - the concentration range over which the ICP analytical curve remains linear.

m/z - Mass to charge ratio, synonymous with "m/e".

MATRIX - the predominant material, component, or substrate (e.g., surface water, drinking water, etc.) of which the sample to be analyzed is composed. Matrix is <u>not</u> synonymous with phase (liquid or solid).

MATRIX DUPLICATE - an intra-laboratory split sample which is used to document the precision of a method in a given sample matrix.

MATRIX MODIFIER - salts used in AA to lessen the effects of chemical interferents, viscosity, and surface tension.

MATRIX SPIKE - aliquot of a sample (water or soil) fortified (spiked) with known quantities of specific compounds (target analytes) and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by

measuring recovery. The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

MATRIX SPIKE BLANK - an aliquot of reagent water fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the spiking solution used for the MS/MSDs.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the Matrix Spike (above) that is spiked with identical concentrations of target analytes as the Matrix Spike, in order to document the precision and bias of the method in a given sample matrix.

MDL - see Method Detection Limit

METHOD BLANK (previously termed reagent blank) - an analytical control sample prepared from an analyte-free matrix to which all reagents, internal standards and surrogate standards are added in the same volumes or proportions as used in sample processing, that is carried through the entire analytical procedure. The method blank is used to document the level of laboratory background and reagent contamination resulting from the analytical process.

METHOD DETECTION LIMIT - the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix type containing the analyte.

For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL shall be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation obtained from a minimum of seven analyses of a matrix spike containing the analyte of interest at a concentration three to five times the estimated MDL, where the t-statistic is obtained from standard references or the table below.

No. of samples:	t-statistic
7	3.14
8	3.00
9	2.90
10	2.82

Estimate the MDL as follows: Obtain the concentration value that corresponds to:

a) an instrument signal/noise ratio within the range of 2.5 to 5.0, or

b) the region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

Determine the variance (S^2) for each analyte as follows:

$$S^2 = \frac{1}{n-1}\left(\sum_{i=1}^{n}(x_i - \bar{x})^2\right)$$

where:

x_i = the ith measurement of the variable x and

$\overline{x}$ = the average value of x;

$$\overline{x} = \frac{1}{n}\left(\sum_{i=1}^{n}(x_i)\right)$$

Determine the standard deviation (s) for each analyte as follows:

$$s = (S^2)^{½}$$

Determine the MDL for each analyte as follows:

$$MDL = t_{(n-1,a=.99)}(s)$$

where $t_{(n-1,a=.99)}$ is the one-sided t-statistic appropriate for the number of samples used to determine (s), at the 99 percent level.

METHOD OF STANDARD ADDITIONS (MSA) - the addition of 3 increments of a standard solution (spikes) to sample aliquots of the same size. Measurements are made on the original and after each addition. The slope, x-intercept and y-intercept are determined by least-square analysis. The analyte concentration is determined by the absolute value of the x-intercept. Ideally, the spike volume is low relative to the sample volume (approximately 10% of the volume). Standard addition may counteract matrix effects; it will not counteract spectral effects. Also referred to as Standard Addition.

MINIMUM QUANTITATION LIMIT - the minimum level that an analyte can be quantitated within a specified precision.

MQL - see Minimum Quantitation Limit

NARRATIVE (SDG Narrative) - portion of the data package which includes laboratory, contract, SDG, Case and sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution. Complete SDG Narrative specifications are included in Exhibit B.

ORGANIC-FREE REAGENT WATER - for volatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated

carbon. A water purification system may be used to generate organic-free deionized water. Organic-free reagent water may also be prepared by boiling water for 15 minutes and, subsequently, while maintaining the temperature at 90°C, bubbling a contaminant-free inert gas through the water for 1 hour.

For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern must be no higher than the highest of either:

1) The detection limit, or

2) Five percent of the regulatory limit for that analyte, or

3) Five percent of the measured concentration in the sample.

For semivolatiles and non-volatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water.

For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern must be no higher than the highest of either:

1) The detection limit, or

2) Five percent of the regulatory limit for that analyte, or

3) Five percent of the measured concentration in the sample.

PERCENT DIFFERENCE (%D) - As used in this Protocol and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference below).

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105°C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

PERCENT SOLIDS - the proportion of solid in a soil sample determined by drying an aliquot of the sample.

PERFORMANCE EVALUATION (PE) SAMPLE - a sample of known composition provided by NYSDEC for contractor analysis. Used by NYSDEC to evaluate Laboratory performance.

PREPARATION BLANK (reagent blank, method blank) - an analytical control that contains distilled, deionized water and reagents, which is carried through the entire analytical procedure (digested and analyzed). An aqueous method blank is treated with the same reagents as a sample with a water matrix. A solid method blank is treated with the same reagents as a soil sample.

PRECISION - the agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV),

$$RSD = CV = 100\left(\frac{S}{\overline{x}}\right)$$

where $\overline{x}$ = the arithmetic mean of the x_i, measurements, and S = variance; and the relative percent difference (RPD) when only two samples are available.

$$RPD = 100\left(\frac{x_1 - x_2}{\left(\frac{(x_1 + x_2)}{2}\right)}\right)$$

PRIMARY ANALYSIS - one of two types of pesticide/PCB analysis by GC/EC techniques, the other being the Confirmation Analysis. If the two analyses are run at separate times, the Primary Analysis is the first analysis chronologically, and is used to establish the tentative identification of any pesticides/PCBs detected. The identification is then confirmed in the confirmation analysis. If the two analyses are run simultaneously, either may be considered the Primary Analysis.

PROJECT - single or multiple data collection activities that are related through the same planning sequence.

PROTOCOL - describes the exact procedures to be followed with respect to sample receipt and handling, analytical methods, data reporting and deliverables, and document control. Used synonymously with Analytical Services Protocol (ASP) and Statement of Work (SOW).

PURGE AND TRAP (DEVICE) - analytical technique (device) used to isolate volatile (purgeable) organics by stripping the compounds from water or soil by a stream of inert gas, trapping the compounds on an adsorbent such as a porous polymer trap, and thermally desorbing the trapped compounds onto the gas chromatographic column.

QUALITY ASSURANCE PROJECT PLAN (QAPJP) - an orderly assemblage of detailed procedures designed to produce data of sufficient quality to meet the data quality objectives for a specific data collection activity.

RCRA - Resource Conservation and Recovery Act

REAGENT BLANK - see Method Blank

REAGENT GRADE - Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER - water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern must be no higher than the highest of either:

1) The detection limit, or

2) Five percent of the regulatory/limit for that analyte, or

3) Five percent of the measured concentration in the sample.

For organic analyses, see the definition of organic-free reagent water.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph; a plot of total ion current versus retention time.

RECOVERY - a determination of the accuracy of the analytical procedure made by comparing measured values for a fortified (spiked) sample against the known spike values. Recovery is determined by the following equation:

$$\%Rec = \frac{\text{measured value}}{\text{known value}} \times 100\%$$

REFERENCE MATERIAL - a material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

RELATIVE PERCENT DIFFERENCE (RPD) - as used in this Protocol and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (in contrast, see percent difference above).

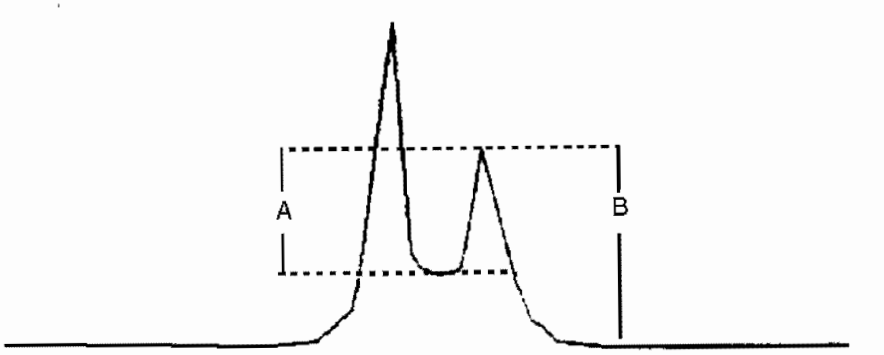
RELATIVE RESPONSE FACTOR (RRF) - a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples. RRF is determined by the following equation:

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

Where:

A = area of the characteristic ion measured
C = concentration
is = internal standard
x = analyte of interest

RESOLUTION - also termed separation, the separation between peaks on a chromatogram, calculated by dividing the depth of the valley between the peaks by the peak height of the smaller peak being resolved, multiplied by 100.



$$\%Resolution = \frac{A}{B} \times 100$$

ROUNDING RULES - if the figure following those to be retained in less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.443 is rounded off to 11.44.

If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded off to 11.45.

If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded off to 11.44, while 11.425 is rounded off to 11.42.

If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

RUN - a continuous analytical sequence consisting of prepared samples and all associated quality assurance measurements as required by the Protocol.

SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

SAMPLE DELIVERY GROUP (SDG) - a unit within a sample Case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer samples within a Case, received over a period of up to 7 calendar days. Data from all samples in an SDG are due concurrently. A Sample Delivery Group is defined by one of the following, whichever occurs first.

- SDG; or
- Each 20 samples within a SDG; or
- Each 7-day calendar period during which samples in a SDG are received, beginning with receipt of the first sample in the SDG.

Samples may be assigned to Sample Delivery Groups by matrix (i.e., all soils in one SDG, all waters in another), at the discretion of the Laboratory.

SAMPLE NUMBER (NYSDEC Sample Number) - a unique identification number designated by NYSDEC for each sample. The NYSDEC sample number appears on the sample Contract Lab Sample Information Sheet which documents information on that sample.

SEMIVOLATILE COMPOUNDS - compounds amenable to analysis by extraction of the sample with an organic solvent. Used synonymously with Base/Neutral/Acid (BNA) compounds.

SDG - see Sample Delivery Group

SERIAL DILUTION - the dilution of a sample by a known factor. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

SOIL - used herein synonymously with soil/sediment or sediment.

SPLIT SAMPLES - aliquots of sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field duplicate samples must be taken for the matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or interlaboratory precision.

STANDARD ADDITION - the practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences.

STANDARD ANALYSIS - an analytical determination made with known quantities of target compounds; used to determine response factors.

STANDARD CURVE - a plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

STOCK SOLUTION - a standard solution which can be diluted to derive other standards.

SURROGATES (Surrogate Standards) - an organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process. For semivolatiles and pesticides/Aroclors, surrogate compounds are added to every blank, sample, matrix spike, matrix spike duplicate, matrix spike blank, and standard. These are used to evaluate analytical efficiency by measuring recovery. Surrogates are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

SYSTEM MONITORING COMPOUNDS - compounds added to every blank, sample, matrix spike, matrix spike duplicate, matrix spike blank, and standard for volatile analysis, and used to evaluate the performance of the entire purge and trap-gas chromatograph-mass spectrometer system. These compounds are brominated or deuterated compounds not expected to be detected in environmental media.

TARGET COMPOUND LIST (TCL) - a list of compounds designated by the Contract Lab Sample Information Sheet and/or the Protocol (Exhibit C) for which the sample is to be analyzed.

TENTATIVELY IDENTIFIED COMPOUNDS (TIC) - compounds detected in samples that are not target compounds, internal standards or surrogate standards. Up to 30 peaks (those greater than 10% of peak areas or heights of nearest internal standards) are subjected to mass spectral library searches for tentative identification.

TIME - when required to record time on any deliverable item, time shall be expressed as Military Time, i.e., a 24-hour clock.

TRIP BLANK - a sample of analyte-free media taken from the Laboratory to the sampling site and returned to the Laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

TOTAL METALS - analyte elements which have been digested prior to analysis.

TWELVE-HOUR TIME PERIOD - the twelve (12) hour time period for GC/MS system instrument performance check, standards calibration (initial or continuing calibration), and method blank analysis begins at the moment of injection of the DFTPP or BFB analysis that the Laboratory submits as documentation of instrument performance. The time period ends after 12 hours has elapsed according to the system clock. For pesticide/Aroclor analyses performed by GC/EC, the twelve hour time period in the

analytical sequence begins at the moment of injection of the instrument blank that precedes sample analyses, and ends after twelve hours have elapsed according to the system clock.

VALIDATED TIME OF SAMPLE RECEIPT (VTSR) - the date on which a sample is received at the Laboratory's facility, as recorded on the shipper's delivery receipt and Chain-of-Custody.

VOLATILE COMPOUNDS - compounds amenable to analysis by the purge and trap technique. Used synonymously with purgeable compounds.

WET WEIGHT - the weight of a sample aliquot including moisture (undried).

WIDE BORE CAPILLARY COLUMN - a gas chromatographic column with an internal diameter (ID) that is greater than 0.32 mm. Columns with lesser diameters are classified as narrow bore capillaries.

10% FREQUENCY - a frequency specification during an analytical sequence allowing for not more than 10 analytical samples between required calibration verification measurements, as specified by the Protocol.

EXHIBIT H

DATA DICTIONARY AND FORMAT FOR DATA DELIVERABLES IN COMPUTER-READABLE FORMAT

SECTION I

DESCRIPTION OF DELIVERABLES

SUPERFUND CLP INORGANICS

See Exhibit D, CLP, Inorganics

SECTION II

DESCRIPTION OF DELIVERABLES

SUPERFUND CLP ORGANICS

See Exhibit D, CLP, Organics

SECTION III

DESCRIPTION OF DELIVERABLES

FOR ALL SAMPLES

IN XBASE III/EXCEL/ASCII FORMAT

The analytical results for all samples submitted by NYSDEC, and all associated Quality Control samples (Method Blanks, MS/MSD/MSBs) must be reported in electronic format utilizing one of the following formats

XBase (dbf)

Microsoft Excel (xls) (Preferred)

ASCII

The Laboratory may use any of these formats. The information will include result and any data qualifier as separate entries for each parameter analyzed and each sample reported.

An example format would be a speadsheet format (Excel) having one row for each parameter analyzed and two columns for each sample reported (one column for the result and one column for the data qualifier.

NYSDEC will work with the Laboratory to set up an acceptable format for both parties data systems.

Part II -- Sample Preservation And Holding Time Requirements

The Laboratory shall adhere to the preservation procedures and holding times listed in Table I below unless specifically directed otherwise by the Bureau of Technical Services and Research or the Project Officer. All holding times are from Verified Time of Sample Receipt (VTSR) at the Laboratory.

The Laboratory shall provide all necessary preservatives to properly stabilize the samples. The Laboratory must adhere to all analytical holding times. Failure to do so will result in the imposition of any contract specified penalties.

Table I - Required Containers, Preservatives, and Holding Times

Parameter Name	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
Aqueous Samples			
Bacteriological Tests:			
Total Coliform	Sterilized P,G	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	6 hours
Fecal Coliform	Sterilized P,G	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	6 hours
Fecal Streptococci	Sterilized P,G	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	6 hours
Inorganic and Conventionals Tests:			
Acidity	P,G	Cool, 4°C	12 days
Alkalinity	P,G	Cool, 4°C	12 days
Ammonia	P,G	Cool, 4°C, H_2SO_4 to pH < 2	26 days
BOD_5	P,G	Cool, 4°C	24 hours
BOD_{20}	P,G	Cool, 4°C	24 hours
Bromide	P,G	Cool, 4°C	26 days

Table I - Required Containers, Preservatives, and Holding Times (Continued)

Parameter Name	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
Aqueous Samples (Continued)			
$CBOD_5$	P,G	Cool, 4°C	24 hours
COD	P,G	Cool, 4°C, H_2SO_4 to pH < 2	26 days
Chloride	P,G	Cool, 4°C	26 days
Color	P,G	Cool, 4°C	24 hours
Cyanide, Total	P,G	Cool, 4°C, NaOH to pH > 12	12 days
Cyanide, Amenable to Chlorination	P,G	Cool, 4°C, NaOH to pH > 12, 0.6 g ascorbic acid[5]	12 days[6]
Fluoride	P only	Cool, 4°C	26 days
Hardness	P,G	HNO_3 to pH < 2	6 months
Kjeldahl Nitrogen	P,G	Cool, 4°C, H_2SO_4 to pH < 2	26 days
Organic Nitrogen	P,G	Cool, 4°C, H_2SO_4 to pH < 2	26 days
Metals[7], except Chromium^{+6} and Mercury	P,G	HNO_3 to pH < 2	6 months
Chromium^{+6}	P,G	Cool, 4°C	24 hours
Mercury	P,G	HNO_3 to pH < 2	26 days

Table I - Required Containers, Preservatives, and Holding Times (Continued)

Parameter Name	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
Aqueous Samples (Continued)			
Nitrate + Nitrite	P,G	Cool, 4°C, H_2SO_4 to pH < 2	26 days
Nitrate	P,G	Cool, 4°C	24 hours
Nitrite	P,G	Cool, 4°C	24 hours
Oil and Grease	G only	Cool, 4°C, H_2SO_4 to pH < 2	26 days
Total Organic Carbon	P,G	Cool, 4°C, H_2SO_4 to pH < 2	26 days
Orthophosphate	P,G	Cool, 4°C	24 hours
Total Phenols	G only	Cool, 4°C, H_2SO_4 to pH < 2	26 days
Phosphorous, Total	P,G	Cool, 4°C, H_2SO_4 to pH < 2	26 days
Residue, Total	P,G	Cool, 4°C	5 days
Residue, Filterable	P,G	Cool, 4°C	24 hours
Residue, Non-Filterable	P,G	Cool, 4°C	5 days
Residue, Settleable	P,G	Cool, 4°C	24 hours
Residue, Volatile	P,G	Cool, 4°C	5 days

Table I - Required Containers, Preservatives, and Holding Times (Continued)

Parameter Name	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
Aqueous Samples (Continued)			
Silica	P only	Cool, 4°C	26 days
Specific Conductance	P,G	Cool, 4°C	26 days
Sulfate	P,G	Cool, 4°C	26 days
Sulfide	P,G	Cool, 4°C,add zinc acetate plus NaOH to pH > 9	5 days
Surfactants (MBAS)	P,G	Cool, 4°C	24 hours
Turbidity	P,G	Cool, 4°C	24 hours
Organic Tests[8]:			
Purgeable Halocarbons	G, Teflon® lined septa	Cool, 4°C 0.008% $Na_2S_2O_3$[5], HCl to pH <2 (Optional)	7 days Unpreserved 10 days Preserved
Purgeable Aromatics	G, Teflon® lined septa	Cool, 4°C 0.008% $Na_2S_2O_3$[5], HCl to pH <2 (Optional)	7 days Unpreserved 10 days Preserved
Acrolein and Acrylonitrile	G, Teflon® lined septa	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], Adjust to pH 4 - 5[9]	7 days
Phenolics[10]	G, Teflon® lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	5 days after VTSR until extraction; 40 days for analysis[12]

Table I - Required Containers, Preservatives, and Holding Times (Continued)

Parameter Name	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
Aqueous Samples (Continued)			
Benzidines[10,11]	G, Teflon® lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	5 days after VTSR until extraction[12]
Phthalate esters[10]	G, Teflon® lined cap	Cool, 4°C,	5 days after VTSR until extraction; 40 days for analysis[12]
Nitrosamines[10,14]	G, Teflon® lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], Store in dark	5 days after VTSR until extraction; 40 days for analysis[12]
PCBs[10]	G, Teflon® lined cap	Cool, 4°C	5 days after VTSR until extraction; 40 days for analysis[12]
Nitroaromatics and Isophorone[10]	G, Teflon® lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], Store in dark	5 days after VTSR until extraction; 40 days for analysis[12]
Polynuclear Aromatic Hydrocarbons[10]	G, Teflon® lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], Store in dark	5 days after VTSR until extraction; 40 days for analysis[12]

Table I - Required Containers, Preservatives, and Holding Times (Continued)

Parameter Name	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
Aqueous Samples (Continued)			
Haloethers[10]	G, Teflon® lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	5 days after VTSR until extraction; 40 days for analysis[12]
Chlorinated Hydrocarbons[10]	G, Teflon® lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5],	5 days after VTSR until extraction; 40 days for analysis[12]
Chlorinated Dioxins and Furans[10]	G, Teflon® lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5],	5 days after VTSR until extraction; 40 days for analysis[12]
Pesticides[10]	G, Teflon® lined cap	Cool, 4°C, Adjust pH to 5 - 9[14]	5 days after VTSR until extraction; 40 days for analysis[12]
Radiological Tests:			
Alpha, beta and Radium	P,G	HNO_3 to pH < 2	6 months

Footnotes for Table I

1. Polyethylene (P) or Glass (G).

2. Sample preservation should be performed immediately upon collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

3. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For preservation requirements of Table I, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric Acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric Acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric Acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium Hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

4. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the monitoring laboratory has data on file to show that specific types of samples under study are stable for the longer time, and has received written permission prior to analysis from the Regional Administrator under 40 CFR Part 136.3(e) AND from the Bureau of Technical Services and Research. Some samples may not be stable for the maximum time period given in the table. A monitoring laboratory is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability.

5. Should only be used in the presence of residual chlorine.

6. Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

7. Samples should be filtered immediately on-site before adding preservative for dissolved metals.

8. Guidance applies to samples to be analyzed by GC, LC or GC/MS for specific compounds.

9. The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

10. When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6 - 9; samples preserved in this manner may be held for five days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re the requirement for thiosulfate reduction of residual chlorine), and footnotes 12, 13 (re the analysis of benzidine).

11. If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ±0.2 to prevent rearrangement of benzidine.

12. This does not supersede the contract requirement of a 30 day reporting time.

13. Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.

14. For the analysis of diphenylnitrosamine, add 0.008% sodium thiosulfate and adjust the pH to 7 - 10 with NaOH within 24 hours of sampling.

15. The pH adjustment may be performed upon receipt in the Laboratory and may be omitted if the samples are extracted with 72 hours of collection. For the analysis of aldrin, add 0.008% sodium thiosulfate.

Soil/Sediment/Solid Samples

The same containers and holding times as listed for aqueous samples are to be used for soil/sediment/solid samples, except for chlorinated dioxins and furans which are allowed 30 days until extraction. Preservation for all analyses is limited to cooling to 4°C.

Toxicity Characteristic Leaching Procedure Samples

	From: VTSR To: TCLP extraction	From: TCLP Extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total Elapsed Time
Volatiles	7	NA	7	14
Semivolatiles	5	7	40	52
Mercury	5	NA	28	33
Metals, except Mercury	180	NA	180	360
NA = Not applicable				

Table 1
40 CFR Part 136
Pollutants in Water

Parameter	Method*	Usage Factor	Cost Per Water Sample Category A Reporting	Cost Per Water Sample Category B Reporting
B/N/A's	625	44	$0.00	$0.00
B/N/A's (Dilution runs only)	625		$0.00	$0.00
Pesticides/PCBs	608	42	$0.00	$0.00
Pesticides/PCBs (Dilution runs only)	608		$0.00	$0.00
PCBs (0.065 µg/L Detection Limit)	608	24	$0.00	$0.00
Volatiles (Purgeable Organics)	624	66	$0.00	$0.00
13 Priority Pollutant Metals (Sb, As, Be, Cd, Cu, Total Cr, Pb, Hg, Ni, Se, Ag, Tl, Zn)	200 Series	99	$0.00	$0.00
Cyanides	335.2	42	$0.00	$0.00
Specific Conductance	120.1		$0.00	$0.00
pH	150.1	14	$0.00	$0.00
Volatiles	601	39	$0.00	$0.00
Aromatic Volatiles	602	79	$0.00	$0.00
Total Organic Carbon	415.1	49	$0.00	$0.00
Soluble Organic Carbon	415.1	49	$0.00	$0.00

* 40 CFR Part 136 as published in Vol 49 Federal Register pg. 43233 - 43442 and Vol 50 Federal Register pg. 689 - 698. Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol - (ASP), as revised 06/2000

Table 1 (continued)
40 CFR Part 136
Pollutants in Water

Parameter	Method*	Usage Factor	Cost Per Water Sample Category A Reporting	Cost Per Water Sample Category B Reporting
BOD_5	405.1	175	$0.00	$0.00
COD	410.1	49	$0.00	$0.00
Total Phenols	420.1	63	$0.00	$0.00
Oil and Grease	413.1	104	$0.00	$0.00
Total Dissolved Solids	160.1	60	$0.00	$0.00
Total Suspended Solids	160.2	198	$0.00	$0.00
Total Solids	160.3	79	$0.00	$0.00
Total Volatile Solids	160.4	121	$0.00	$0.00
Total Settleable Solids	160.5	46	$0.00	$0.00
Turbidity	180.1	6	$0.00	$0.00
MBAS	425.1	26	$0.00	$0.00
TKN	351.3	207	$0.00	$0.00
Ammonia	350.2	225	$0.00	$0.00
Nitrate-Nitrite	353.2	174	$0.00	$0.00
Total Phosphorous	365.3	156	$0.00	$0.00
Reactive Phosphorous	365.3	18	$0.00	$0.00
Sulfate	375.4	57	$0.00	$0.00
Sulfide	376.1, 376.2	3	$0.00	$0.00
Total Hardness	130.1,130.2	52	$0.00	$0.00
Bromide	320.1	30	$0.00	$0.00
Chloride	325.1, 325.2, 325.3	63	$0.00	$0.00
Fluoride	340.1, 340.2, 340.3	36	$0.00	$0.00

* 40 CFR Part 136 as published in Vol 49 Federal Register pg. 43233 - 43442 and Vol 50 Federal Register pg. 689 - 698. Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 06/2000

Table 1 (continued)
40 CFR Part 136
Pollutants in Water

Parameter	Method*	Usage Factor	Cost Per Water Sample Category A Reporting	Cost Per Water Sample Category B Reporting
Metals	200 Series			
Antimony	"		$0.00	$0.00
Arsenic	"	5	$0.00	$0.00
Barium	"		$0.00	$0.00
Beryllium	"	3	$0.00	$0.00
Boron	"	30	$0.00	$0.00
Cadmium	"	8	$0.00	$0.00
Calcium	"		$0.00	$0.00
Hexavalent Chromium	"	28	$0.00	$0.00
Total Chromium	"	6	$0.00	$0.00
Cobalt	"		$0.00	$0.00
Copper	"	18	$0.00	$0.00
Iron	"	39	$0.00	$0.00
Lead	"	15	$0.00	$0.00
Magnesium	"		$0.00	$0.00
Mercury	"	9	$0.00	$0.00
Nickel	"	11	$0.00	$0.00
Potassium	"		$0.00	$0.00
Selenium	"		$0.00	$0.00
Silver	"	7	$0.00	$0.00
Sodium	"	6	$0.00	$0.00
Strontium	"		$0.00	$0.00
Thallium	"	3	$0.00	$0.00
Tin	"		$0.00	$0.00
Vanadium	"	1	$0.00	$0.00
Zinc	"	27	$0.00	$0.00

* 40 CFR Part 136 as published in Vol 49 Federal Register pg. 43233 - 43442 and Vol 50 Federal Register pg. 689 - 698. Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 06/2000

Table 2
SW846 - Water

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Volatile Organics	8010	22	$0.00	$0.00
Nonhalogenated Volatile Organics	8015		$0.00	$0.00
Volatile Aromatics	8020	12	$0.00	$0.00
Volatile Organics	8021		$0.00	$0.00
Phenolics	8040	2	$0.00	$0.00
Pesticides/PCBs	8081	10	$0.00	$0.00
Pesticides/PCBs (Dilutions only)	8081		$0.00	$0.00
Volatile Organics GC/MS	8260	52	$0.00	$0.00
B/N/As	8270	14	$0.00	$0.00
B/N/As (Dilution runs only)	8270		$0.00	$0.00
Polynuclear Aromatic Hydrocarbons	8100 or 8310		$0.00	$0.00
Organophosphorous Pesticides (Capillary Column)	8141	3	$0.00	$0.00
Chlorophenoxy Acid Herbicides	8150	3	$0.00	$0.00
17 Hazardous Metals - Sb, As, Ba, Be, Cd, Total Cr, Co, Cu, Pb, Hg, Ni, Se, Ag, Tl, Sn, V, Zn	6010, 7000 Series	11	$0.00	$0.00
Cyanide	9010	7	$0.00	$0.00
Sulfide	9030	1	$0.00	$0.00
pH	9040		$0.00	$0.00
Total Organic Halogen	9020		$0.00	$0.00
Total Organic Carbon	9060		$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 06/2000

Table 2 (continued)
SW846 - Water

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Corrosivity (pH only)	Section 2.1.1	1	$0.00	$0.00
Corrosivity (Nace)	Section 2.1.1		$0.00	$0.00
Ignitability	Section 2.1.2		$0.00	$0.00
Reactivity	Section 2.1.3	1	$0.00	$0.00
Extraction Procedure Toxicity (Extraction Only)	Section 2.1.4	1	$0.00	$0.00
Full Appendix IX (NYS Appendix 33) (not including Dioxin)		19	$0.00	$0.00
Toxicity Characteristic Leaching Procedure:				
Metals and Semivolatile Extract Preparation	See ASP	1	$0.00	$0.00
Zero Headspace Volatile Extract Preparation	See ASP	2	$0.00	$0.00
TCLP Metals - As, Ba, Cd, Total Cr, Pb, Hg, Se, Ag	See ASP	1	$0.00	$0.00
IR Scan	See ASP		$0.00	$0.00
Cleanups				
Alumina Cleanup	3610		$0.00	$0.00
Forisil Cleanup	3620		$0.00	$0.00
Silica Gel Cleanup	3630		$0.00	$0.00
Gel-Permeation Cleanup	3640		$0.00	$0.00
Acid-Base Partition Cleanup	3650		$0.00	$0.00
Sulfur Cleanup	3660		$0.00	$0.00
Sulfuric Acid Cleanup	3665A		$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 06/2000

Appendix C

Standard Forms and Checklists

Figure 7-4

QUALITY CONTROL FIELD AUDIT REPORT

SUMMARY INFORMATION

1. PROJECT NAME: _____

2. PROJECT ADDRESS: _____

_____

_____

3. PRELIMINARY ASSESSMENT _____ RI/FS _____ RD _____ CONSTRUCTION_____

OTHER _____

4. DATE(S) OF QC FIELD AUDIT _____

5. AUDITOR'S NAME _____PHONE_____

6. FACILITY CONTACT _____PHONE_____

7. CONTRACTOR CONTACT_____PHONE_____

8. PERSONNEL ON-SITE

NAME	REPRESENTING	PHONE

9. AUDITOR'S COMMENTS

_____

_____

_____

_____

10. WEATHER CONDITIONS

SUNNY ; PARTLY SUNNY ; PARTLY CLOUDY ; CLOUDY ; RAIN ; DRIZZLE ; SNOW ; SLEET

TEMPERATURE_____ WIND SPEED_____ WIND DIRECTION_____

11. LEVEL OF PERSONNEL PROTECTION REQUIRED IN WORK PLAN

A B C D

LEVEL OF PERSONNEL PROTECTION ACTUALLY DONNED:

A B C D

12. FIELD SURVEY EQUIPMENT

INSTRUMENT	MODEL	CALIBRATION CHECK	CALIBRATION STANDARD	SPAN SETTING
CONDUCTIVITY METER				
DISSOLVED O_2 METER				
PH METER				
COMBUSTIBLE GAS INDICATOR (LEL/O_2)				
FLAME IONIZATION DETECTOR (OVA)				
PHOTOIONIZATION DETECTOR (HNU)				
TOTAL GAS INDICATOR (CO,H_2S)				
OTHER				

OBSERVATIONS _____

_____

_____

13. DID THE SAMPLING TEAM TAKE PERIODIC SURVEYS OF THE AMBIENT AIR CONDITIONS?

YES NO N/A

14. DID THE SAMPLING TEAM PROVIDE A DECON ZONE DESIGNATING CLEAN AND CONTAMINATED AREAS?

YES NO N/A

15. WERE PHOTOGRAPHS TAKEN? YES NO

16. AUDITOR'S COMMENTS

_____

_____

_____

MONITORING WELL SAMPLING SETUP AND EVACUATION

EVACUATION PROCEDURES

1. WELL CASING CONSTRUCTION STAINLESS STEEL TEFLON PVC OTHER _____

2. DIAMETER OF WELL CASING 2" 4" 6" OTHER _____

3. LOCKING CAPS ON THE WELLS? YES NO N/A PROTECTIVE CASING? YES NO N/A

4. METHOD UTILIZED TO DETERMINE THE STATIC WATER LEVEL

WATER LEVEL INDICATOR OTHER _____

5. REFERENCE POINT THAT THE STATIC WATER LEVEL WAS MEASURED FROM:

SURVEY POINT	TOP OF INNER CASING	TOP OF PROTECTIVE CASING	HEIGHT OF CASING ABOVE GROUND SURFACE

6. WAS THE WATER LEVEL INDICATOR DECONTAMINATED ACCORDING TO STANDARD PROCEDURES BETWEEN EACH WELL?
YES NO N/A

IF NO, METHOD USED: _____

_____

_____

7. EVACUATION METHOD:

BAILER CENTRIFUGAL PUMP PERISTALTIC PUMP BLADDER PUMP SUBMERSIBLE PUMP

GAS DISPLACEMENT PUMP GAS LIFT PUMP OTHER _____

8. TYPE OF HOSE UTILIZED:

POLYETHYLENE TEFLON SILASTIC N/A OTHER _____

9. WAS THE HOSE DEDICATED TO EACH WELL LOCATION? YES NO N/A

IF NO, METHOD OF DECONTAMINATION _____

10. WAS THE PUMP DEDICATED TO EACH WELL LOCATION? YES NO N/A

11. WAS THE PUMP: LABORATORY DECONTAMINATED? FIELD DECONTAMINATED? N/A

12. WAS THE PUMP DECONTAMINATED ACCORDING TO STANDARD PROCEDURES?

YES NO IF NO, METHOD OF DECONTAMINATION _____

13. WAS THE PUMP HEAD OR END OF HOSE WITHIN 6 FEET OF THE DYNAMIC WATER LEVEL DURING EVACUATION?
YES NO N/A

14. WAS THE DECONTAMINATION AREA LOCATED AWAY FROM THE SOURCE OF CONTAMINATION?

YES NO N/A

15. AUDITOR'S COMMENTS

_____

_____

_____

AQUEOUS SAMPLING PROCEDURES

1. AQUEOUS MATRIX SAMPLED:

POTABLE WELL GROUND WATER SURFACE WATER LEACHATE RUNOFF STORM SEWER

SANITARY SEWER OTHER _____

2. TYPE OF SAMPLE: GRAB COMPOSITE IF COMPOSITE - SAMPLES/COMPOSITE _____

3. WAS THE VOA SAMPLE COLLECTED FIRST? YES NO N/A

4. TYPE OF SAMPLING EQUIPMENT:

	MATERIAL OF CONSTRUCTION			
	STAINLESS STEEL	TEFLON	GLASS	OTHER
BAILER	_____	_____	_____	_____
BLADDER PUMP	_____	_____	_____	_____
SAMPLER	_____	_____	_____	_____
COLIWASA	_____	_____	_____	_____
KEMMERER DEPTH SAMPLER	_____	_____	_____	_____
WHEATON DIP SAMPLER	_____	_____	_____	_____
TUB SAMPLER	_____	_____	_____	_____
BACON BOMB	_____	_____	_____	_____

5. TYPE OF LEADER LINE THAT COMES IN CONTACT WITH THE WELL WATER:

TEFLON TEFLON COATED STAINLESS STEEL N/A OTHER _____

6. LENGTH OF THE LEADER LINE _____

7. WAS THE SAMPLING EQUIPMENT DEDICATED? YES _____ NO _____

8. WAS THE SAMPLING EQUIPMENT: LAB DECONTAMINATED? FIELD DECONTAMINATED?

9. WAS THE SAMPLING EQUIPMENT DECONTAMINATED ACCORDING TO STANDARD PROCEDURES?

YES NO IF NO, METHOD OF DECONTAMINATION: _____

10. WAS THE DECONTAMINATION AREA LOCATED AWAY FROM THE SOURCE OF CONTAMINATION?

YES NO

11. ARE DISPOSABLE GLOVES WORN AND CHANGED BETWEEN EACH SAMPLE LOCATION? YES NO

12. AUDITOR'S COMMENTS:

_____

_____

_____

FIGURE 7-5

NONCONFORMANCE AND CORRECTIVE ACTION REPORT

Date _____

NCR No. _____

Description of Nonconformance and Cause _____

_____

_____

_____

_____

_____

Proposed Disposition _____

_____

_____

_____

_____

_____

Submitted by: _____ Date: _____
Approved by: _____

DISPOSITION (by Project Manager or Designee)

Implementation of Disposition Assigned to: _____

Actual Disposition _____

_____

_____

_____

_____

_____

Disposition completed on: _____
Date

_____
Signature

VERIFICATION
Disposition reviewed and work inspected by: _____ on _____
Disposition verified by: _____ on _____
(Use additional sheet or memo if necessary)

FIGURE 10-1

DATE _____

MMRP: (Installation name)
DAILY QUALITY CONTROL REPORT

DAY	S	M	T	W	TH	F	S

USACE PROJECT MGR. _____

PROJECT _____

JOB NO. _____

CONTRACT NO. _____

WEATHER	BRIGHT SUN	CLEAR	OVERCAST	RAIN	SNOW
TEMPERATURE	< 32	32 - 50	50 - 70	70-85	>85
WIND	STILL	MODERATE	HIGH	REPORT NO.	
HUMIDITY	DRY	MODERATE	HUMID		

SUBCONTRACTORS ON-SITE:
EQUIPMENT ON SITE:
WORK PERFORMED (INCLUDING SAMPLING):
QUALITY CONTROL ACTIVITIES (INCLUDING FIELD CALIBRATIONS):
HEALTH AND SAFETY LEVELS AND ACTIVITIES:
PROBLEMS ENCOUNTERED/CORRECTIVE ACTION TAKEN:
SPECIAL NOTES:
TOMORROW'S EXPECTATIONS:

BY _____ TITLE _____

QA/QC INFORMATION

1. LABORATORY:

NAME _____ PHONE _____

CONTACT PERSON _____

CLP CLP CAPABLE CERTIFIED OTHER _____

3. SAMPLE INFORMATION:

MATRIX	PARAMETER	PRESERVATIVE	CONTAINER DESCRIPTION

3. WHAT ORDER BY ANALYTICAL PARAMETER ARE SAMPLES COLLECTED: _____

_____

4. FIELD BLANKS: YES NO N/A FREQUENCY _____

METHOD: _____

WAS IDENTICAL BOTTLE TO BOTTLE TRANSFER OF WATER UTILIZED? YES NO

5. TRIP BLANKS: YES NO N/A FREQUENCY _____

6. WHAT WAS THE SOURCE OF THE BLANK WATER? LABORATORY DEMONSTRATED ANALYTE-FREE
OTHER_____

7. SAMPLE PACKAGING AND HANDLING:

SAMPLE CONTAINERS LABELED	YES	NO	N/A
COC FORMS COMPLETED	YES	NO	N/A
CUSTODY SEALS	YES	NO	N/A
SAMPLES PRESERVED TO 4°C:	YES	NO	N/A

8. AUDITOR'S COMMENTS

_____

_____

_____

_____

AFCEE
SCREENING DATA SHEET 1
DATA PACKAGE

Analytical Method: _____ **Contract #:** _____

Base/Command: _____ **Prime Contractor:** _____

Field Sample ID

Comments:

_____
_____
_____

Signature: _____ Name: _____

Date: _____ Title: _____

AFCEE FORM S-1

AFCEE
SCREENING DATA SHEET 2
RESULTS

Analytical Method: _____

Contract #: _____ **Field Sample ID:** _____

Matrix: _____ **Date Analyzed:** _____

Concentration Units (µg/L, mg/kg dry weight or °C): _____

Analyte/Test	MDL	RL	Result	Qualifier

Comments: _____

AFCEE FORM S-2 Page _____ of _____

AFCEE
SCREENING DATA SHEET 3
FIELD DUPLICATES

Analytical Method: _____ **Contract #:** _____

Units: _____

Analyte/Test	Sample Result	Duplicate Sample Result	%D or %RPD	Acceptance Criteria	Q

Comments:_____
_____
_____

AFCEE FORM S-3 Page _____ of _____

PREDRILLING/SUBSURFACE CHECKLIST FOR INTRUSIVE FIELDWORK

Site Name: _____ **Job Number:** _____
Site Phone Number: _____
Site Address: _____ **County:** _____
Client Proj. Mgr.: _____ **Phone:** _____
Site Manager Contacted Date: _____ **By:** _____
Site Drawings (yes / no / NA) _____ (please attach) **Historical Drawings (yes / no / NA)** _____
Third Party Construction/Redevelopment Plans (Yes/No/NA)

*****ATTACH SITE FIGURE WITH PROPOSED BORING LOCATIONS**

Subcontractor's (drillers, concrete, etc…) **Company** _____
Subcontractor's Contact Person _____ **Phone** _____
Meeting / Start Date _____ **Time** _____

1) Health and Safety Signoff Form Completed? (Yes/No) **Date** _____

2) Utility Protection Services (Minimum 48 Hrs. Advance Notice, State Specific Notification Period Supercedes)
Called: Date _____ **Time** _____ **Initials** _____
Reference # _____
Proposed Drilling Locations Premarked for Locating Service. **Y / N**

3) Private or In-House Utility Locating Service Performed? **Y / N** _____
Called: Date _____ **Time** _____ **Initials** _____
Name of Locating Service: _____
Telephone #/ contact: _____
Name of Supplier Locating Technician: _____
Type of sensing equipment used: _____
Proposed Drilling Locations Premarked **Y / N**

4) Other Potential Underground Structures
Name of City Engineer/Utility Representative: _____
Telephone #: _____
Date Notified _____ **Maps:** **Y / N**
Cleared: **Y / N**

5) COMPLETED SITE WALKOVER W/ SITE MANAGER/DESIGNEE OR OWNER/TENANT REP. **Y / N**
Name of Site Manager: _____
Name of Property Owner/Tenant Representative: _____
Cleared: **Yes / No**
Building Utility Service Line Connections Identified: **Y / N**
(Hand sketch on site map w/proposed boring locations and most likely utility trench locations)

6) Utility Inventory: **Y / N**

Utility	Name	Depth (ft) (If Available)	Phone	Notified - Date	Marked
Above Ground Services					
Electric		NA		Y / N	Y / N
Telephone		NA		Y / N	Y / N
Cable		NA		Y / N	Y / N
Overhead Supports		NA		Y / N	Y / N
Traffic light cables		NA		Y / N	Y / N

PREDRILLING/SUBSURFACE CHECKLIST FOR INTRUSIVE FIELDWORK

6) Utility Inventory Continued:

Below Ground Services:

Electric				Y / N		Y / N
Telephone				Y / N		Y / N
Cable				Y / N		Y / N
Gas				Y / N		Y / N
Water				Y / N		Y / N
UST System				Y / N		Y / N
Storm				Y / N		Y / N
Sanitary				Y / N		Y / N
Steam				Y / N		Y / N
Pipeline Companies				Y / N		Y / N

Other:

				Y / N		Y / N
				Y / N		Y / N
				Y / N		Y / N

7) **Site-Specific Emergency Contingency Plan Incorporated in Health & Safety Plar** **Y / N**

8) **Drilling Locations Approved by Client Project Manager Named Above?** **Y / N**

9) **Signature of Parsons' Project Mgr. (required to begin fieldwork):**

Name of Project Manager	**Signature of Project Manager**
Name of Parsons Field Personnel	**Signature of Field Personnel**

(This document to be included with the site H&S Plan and should be available upon request.)

ADDITIONAL COMMENTS / NOTES:

SLUG TEST REPORT FORM

PARSONS | **CLIENT: USACOE** | **WELL #: MW**

PROJECT: RI FIELD INVESTIGATION
WMU # (AREA SEAD-
SOP NO.:

INSPECTOR:
TEST DATE:
WEATHER:
CHECKED BY:

WELL AND AQUIFER INFORMATION

WELL POINT (installed):
WELL CASING INNER DIAMETER:
BOREHOLE DIAMETER:
STATIC DEPTH TO WATER:
SCREENED INTERVAL - FROM:
TO:
(all depths measured from TOC, or taken from installation detail)

WELL SCREEN SLOT SIZE:
AQUIFER THICKNESS:
PRODUCT PRESENT (Y/N?)

TEST EQUIPMENT SPECIFICATIONS

DATA LOGGER BRAND:
INSTRUMENT MODEL:
TRANSDUCER BRAND:

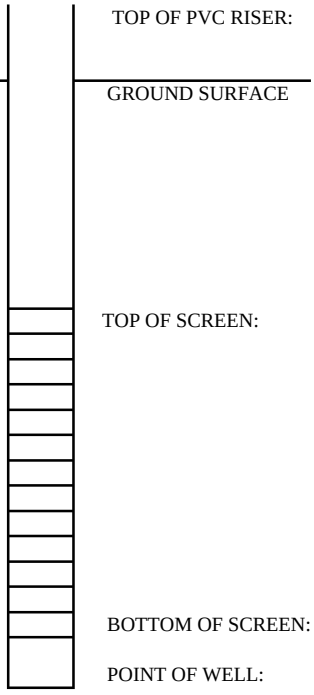
TRANSDUCER RATING (PSI):
SLUG/BAILER DIMENSIONS:
SLUG/BAILER VOLUME:

TEST INFORMATION

REFERENCE VALUE:
TRANSDUCER MOD SURFACE LEVEL or TOC
STATIC WATER (START):
START TIME:
END TIME:
STATIC WATER (END):
ELAPSED TIME:

DATA LOGGER TEST NUMBER:
TRANSDUCER DEPTH:
TRANSDUCER - LINEARITY:
- SCALE:
- OFFSET:
- DELAY:
SATURATED SCREEEN LENGTH:

NOTES:



(ALL DEPTHS RELATIVE TO THE TOP OF PVC CASING)

COMMENTS:

CONVERSION: 2.3O667 FEET OF WATER/PSI

YOU MUST RESET THE REFERENCE VALUE PRIOR TO BEGINNING EACH TEST!!!!!

PARSONS
TEST PIT RECORD

Project Name: _____
Project Number: _____
Date / Time Start: _____
Date / Time Finish: _____
Weather: _____
Contractor: _____
Inspector(s): _____

TEST PIT NO.
Location: _____

DEPTH (ft bgs)	Stratigraphy	Macro	FIELD IDENTIFICATION OF MATERIAL	COMMENTS
_0 ___1 ___2 ___3 ___4 ___5 ___6 ___7 ___8 ___9 ___10				

EXCAVATION DIMENSIONS: (Length X Width X Depth) _____
AIR MONITORING DATA: Background OVM Reading: _____
Maximum Breathing Zone OVM Reading: _____

TIME	SAMPLE I.D.	LOCATION

Analysis Requested:

CROSS SECTION
(Include approximate dimensions)

PAGE 1 OF

OVERBURDEN BORING REPORT

PARSONS	CLIENT:	BORING NO.:

PROJECT : _____

SWMU # (AREA) : _____

SOP NO.: _____

START DATE: _____

FINISH DATE: _____

CONTRACTOR: _____

DRILLER: _____

INSPECTOR: _____

CHECKED BY: _____

CHECK DATE: _____

BORING CONVERTED TO MW? Y N

DRILLING SUMMARY

DRILLING METHOD	HOLE DIA.(ft)	DEPTH INTERVAL (ft)	SAMPLER SIZE	SAMPLER TYPE	HAMMER TYPE	HAMMER WT/FALL

DRILLING ACRONYMS

HSA	HOLLOW-STEM AUGERS	HMR	HAMMER	SS	SPLIT SPOON
DW	DRIVE-AND-WASH	SHR	SAFETY HAMMER	CS	CONTINUOUS SAMPLING
MRSLC	MUD-ROTARY SOIL-CORING	HHR	HYDRAULIC HAMMER	5I	5 FT INTERVAL SAMPLING
CA	CASING ADVANCER	DHR	DOWN-HOLE HAMMER	NS	NO SAMPLING
SPC	SPIN CASING	WL	WIRE-LINE	ST	SHELBY TUBE
				3S	3 INCH SPLIT SPOON

MONITORING EQUPMENT SUMMARY

INSTRUMENT TYPE	DETECTOR TYPE/ENERGY	RANGE	BACKGROUND READING	BACKGROUND TIME	BACKGROUND DATE	CALIBRATION TIME	CALIBRATION DATE	WEATHER (TEMP., WIND, ETC.)

MONITORING ACRONYMS

PID	PHOTO - IONIZATION DETECTOR	BGD	BACKGROUND	DGRT	DRAEGER TUBES
FID	FLAME - IONIZATION DETECTOR	CPM	COUNTS PER MINUTE	PPB	PARTS PER BILLION
GMD	GEIGER MUELLER DETECTOR	PPM	PARTS PER MILLION	MDL	METHOD DETECTION LIMIT
SCT	SCINTILLATION DETECTOR	RAD	RADIATION METER		

INVESTIGATION DERIVED WASTE

DATE			
SOIL AMOUNT : (fraction of drum)			
DRUM #, LOCATION:			

COMMENTS:

SAMPLES TAKEN:

SAMPLES _____

DUPLICATES _____

MS/MSD _____

MRD

PAGE OF

OVERBURDEN BORING REPORT

PARSONS	CLIENT:	BORING NO.:
COMMENTS:		DRILLER: _____
		INSPECTOR: _____
		DATE:

DEPTH (FT)	SAMPLING			SAMPLE				SAMPLE DESCRIPTION (As per Burmeister: color, grain size, MAJOR COMPONENT, Minor Components with amount modifiers and grain-size, density, stratification, wetness, etc.)	USCS CLASS	STRATUM CLASS
	BLOWS PER 6 INCHES	PENE-TRATION RANGE (FEET)	RECOV-ERY RANGE (FEET)	DEPTH INT (FEET)	NO.	VOC	RAD SCRN			

CORE BORING REPORT

PARSONS	CLIENT: USACOE	BORING #:

PROJECT: _____

SWMU # (AREA) : _____

SOP NO.:

DATE CORING STARTED: _____

DATE CORING COMPLETED: _____

CONTRACTOR: _____

DRILLER: _____

INSPECTOR: _____

GEOLOGIST: _____

CHECKED BY: _____

DATE CHECKED: _____

TOTAL FOOTAGE CORED: _____

OVERBURDEN THICKNESS: _____

GALLONS OF WATER USED

MONITORING

INTRUMENT	INTERVAL	BACKGROUND	TIME

COMMENTS:

CORE EQUIPMENT BARREL LENGTH (ft):

TYPE	SERIES	RANGE	O.D.	I.D.

DEPTH FEET	RUN # RANGE FEET	CORE RECOVERY FEET	MON. DATA	RQD %	SCHEMATIC STRATA/ FRACTURES	ANGLES DIP/STRIKE (BD,FL,JNT,FC)	BEDROCK/ CORE DESCRIPTIONS AND REMARKS (color, major modifiers, rock type, minor components, bedding or foliation, strike of joints/fractures relative to foliation, weathering on fractures, etc.)

INVESTIGATION DERIVED WASTE :

DATE			
SOIL AMOUNT (fraction of drum)			
DRUM #, LOCATION			

OVERBURDEN MONITORING WELL
COMPLETION REPORT & INSTALLATION DETAIL
PROTECTIVE RISER COMPLETION

PARSONS	CLIENT:	WELL #:

PROJECT: _____ PROJECT NO: _____

LOCATION: _____ INSPECTOR: _____

CHECKED BY: _____

DRILLING CONTRACTOR: _____ POW DEPTH: _____

DRILLER: _____ INSTALLATION STARTED: _____

DRILLING COMPLETED: _____ INSTALLATION COMPLETED: _____

BORING DEPTH: _____ SURFACE COMPLETION DATE: _____

DRILLING METHOD(S): _____ COMPLETION CONTRACTOR/CREW: _____

BORING DIAMETER(S): _____ BEDROCK CONFIRMED (Y/N?) _____

ASSOCIATED SWMU/AOC: _____ ESTIMATED GROUND ELEVATION: _____

PROTECTIVE SURFACE CASING:

DIAMETER: _____ LENGTH: _____ TOR: _____

RISER:

TOC: _____ TYPE: _____ DIAMETER: _____ LENGTH: _____

SCREEN: SLOT

TSC: _____ TYPE: _____ DIAMETER: _____ LENGTH: _____ SIZE: _____

POINT OF WELL: (SILT SUMP)

TYPE: _____ BSC: _____ POW: _____

GROUT:

TG: _____ TYPE: _____ LENGTH: _____

SEAL: TBS: _____ TYPE: _____ LENGTH: _____

SAND PACK: TSP: _____ TYPE: _____ LENGTH: _____

SURFACE COLLAR:

TYPE: _____ RADIUS: _____ THICKNESS CENTER: _____ THICKNESS EDGE: _____

CENTRALIZER DEPTHS

DEPTH 1: _____ DEPTH 2: _____ DEPTH 3: _____ DEPTH 4: _____

COMMENTS:

* ALL DEPTH MEASUREMENTS REFERENCED TO GROUND SURFACE

SEE PAGE 2 FOR SCHEMATIC

BEDROCK MONITORING WELL
COMPLETION REPORT & INSTALLATION DETAIL
PROTECTIVE RISER COMPLETION

PARSONS	CLIENT: USACOE	WELL #: MW

PROJECT: _____ PROJECT NO: _____

SWMU # (AREA): _____ INSPECTOR: _____

SOP NO.: _____ CHECKED BY: _____

DRILLING CONTRACTOR: _____ POW DEPTH (ft) : _____

DRILLER: _____ INSTALLATION STARTED: _____

DRILLING COMPLETED: _____ INSTALLATION COMPLETED: _____

BORING DEPTH: _____ SURFACE COMPLETION DATE: _____

DRILLING METHOD(S): _____ COMPLETION CONTRACTOR/CREW: _____

BORING DIAMETER(S): _____ BEDROCK CONFIRMED (Y/N?) _____

PROTECTIVE SURFACE CASING

DIAMETER (ft): _____ LENGTH (ft): _____

RISER

TYPE: _____ TR (ft): _____

DIAMETER(in): _____ LENGTH (ft): _____

SURFACE COLLAR

TYPE: _____ RADIUS (ft): _____

THICKNESS OF CENTER (ft): _____ THICKNESS OF EDGE (in) _____

SCREEN

TYPE: _____ TSC (ft): _____

DIAMETER (in): _____ SLOT SIZE: _____ LENGTH (ft): _____

OUTER CASING

TYPE: _____ TC (ft): _____

DIAMETER (in): _____ POC (ft): _____ LENGTH (ft): _____

POINT OF WELL (SILT SUMP)

TYPE: _____ BSC (ft): _____ POW(ft): _____

GROUT

TYPE: _____ TG (ft): _____ LENGTH (ft): _____

SEAL

TYPE: _____ TBS (ft): _____ LENGTH (ft): _____

SAND PACK

FINE SAND TYPE: _____ TSP (ft): _____ LENGTH (ft): _____

COARSE SAND TYPE: _____ TSP (ft): _____ LENGTH (ft): _____

ACRONYMS

TR	Top of Riser	BSC	Bottom of Screen	TG	Top of Grout
TSC	Top of Screen	POW	Point of Well	TBS	Top of Bentonite Seal
BGD	Background	TSP	Top of Sand Pack		

COMMENTS:

* ALL DEPTH MEASUREMENTS REFERENCED TO GROUND SURFACE

WELL DEVELOPMENT REPORT

Page 1 of

PARSONS	CLIENT : USACOE	WELL #: MW

PROGRAM TYPE :	CREW INITIALS	START DATE	END DATE
SWMU # (AREA) :			
PROJECT NO. (JOB #):			

DRILLING DATE:	MONITORING	BEFORE DEVELOPMENT		AFTER DEVELOPMENT	
INSTALLATION DATE:	INSTRUMENT	OVM	RAD	OVM	RAD
SOP REFERENCE NO. & REV. NO. :	READING				
PUMP EQUIPMENT:	UNITS (ppm or cps)				

WELL TYPE (circle one)	BEDROCK	OVERBURDEN	MEASURED WATER DEPTH (feet from TOC):
WELL INNER RISER DIAMETER (inches)	2	2	MEASURED POW DEPTH (feet from TOC):
WELL DIAMETER FACTOR (gal/ft)	0.163	0.163	WATER COLUMN (feet) :
BORING DIAMETER (inches)	3.80	8.5	INSTALLED WATER DEPTH (feet from TOC):
BORING DIAMETER FACTOR (gal/ft)	0.5894	2.955	INSTALLED POW DEPTH (feet from TOC):

1. STANDING VOLUME INSIDE WELL = WATER COLUMN X WELL DIAMETER FACTOR = _____ GAL. = A

2. STANDING WATER IN ANNULAR SPACE =
WATER COLUMN BELOW SEAL(ft) X (BORING DIAMETER FACTOR - WELL DIAMETER FACTOR) X 0.3 = _____ GAL. = B

3. SINGLE STANDING WATER VOLUME = A + B _____ GAL. = C

4. MINIMUM VOLUME TO BE REMOVED = 3 X C _____ GALS.

DATE	ACTIVITY	START TIME (military)	END TIME (military)	GALLONS REMOVED PER TIME PERIOD	pH	CONDUCTIVITY (umhos/cm)	TEMPERATURE (degrees C)	TURBIDITY (NTUs)
	TOTALS/FINAL							

COMMENTS:

INVESTIGATION DERIVED WASTE (IDW) :

DATE			
GALLONS OF WASTE WATER			
DRUM NO. & LOCATION			

PAGE OF

GROUNDWATER ELEVATION REPORT

PARSONS	CLIENT:	DATE:
PROJECT: _____		PROJECT NO: _____
LOCATION: _____		INSPECTOR: _____

MONITORING EQUIPMENT:					WATER LEVEL INDICATOR:		COMMENTS:
INSTRUMENT	DECTECTOR	BGD	TIME	REMARKS	INSTRUMENT	CORRECTION FACTOR	

WELL	TIME	DEPTH TO WATER	DEPTH TO PRODUCT	CORRECTED WATER LEVEL	MEASURED POW	INSTALLED POW	PRODUCT SPEC. GRAV.	WELL STATUS / COMMENTS (Lock?, Well #?, Surface Disturbance?, Riser marked?, Condition of: riser, concrete, protective casing, etc.)

(ALL DEPTH MEASUREMENTS FROM MARKED LOCATION ON RISER)

SAMPLING RECORD - GROUNDWATER

SENECA ARMY DEPOT ACTIVITY	PARSONS	WELL #:

PROJECT: _____ DATE: _____
LOCATION: _____ INSPECTORS: _____
PUMP #: _____
SAMPLE ID #: _____

WEATHER / FIELD CONDITIONS CHECKLIST (RECORD MAJOR CHANGES)

TIME (24 HR)	TEMP (APPRX)	WEATHER (APPRX)	REL. HUMIDITY (GEN)	WIND VELOCITY (APPRX)	(FROM) DIRECTION (0 - 360)	GROUND / SITE SURFACE CONDITIONS	MONITORING INSTRUMENT	MONITORING DETECTOR
							OVM-580	PID

WELL VOLUME CALCULATION FACTORS

DIAMETER (INCHES):	0.25	1	2	3	4	6
GALLONS / FOOT:	0.0026	0.041	0.163	0.367	0.654	1.47
LITERS/FOOT	0.010	0.151	0.617	1.389	2.475	5.564

ONE WELL VOLUME (GAL) = [(POW - STABILIZED WATER LEVEL) X WELL DIAMETER FACTOR (GAL/FT)]

HISTORIC DATA	DEPTH TO POINT OF WELL (TOC)	DEPTH TO TOP OF SCREEN (TOC)	SCREEN LENGTH (FT)	WELL DEVELOPMENT TURBIDITY	WELL DEVELOPMENT pH	WELL DEVELOPMENT SPEC. COND
DATA COLLECTED AT WELL SITE	PID READING (OPENING WELL)	DEPTH TO STATIC WATER LEVEL (TOC)		DEPTH TO STABILIZED WATER LEVEL (TOC)	DEPTH TO PUMP INTAKE (TOC)	PUMPING START TIME
RADIATION SCREENING DATA	PUMP PRIOR TO SAMPLING (cps)			PUMP AFTER SAMPLING (cps)		

MONITORING DATA COLLECTED DURING PURGING OPERATIONS

TIME (min)	WATER LEVEL	PUMPING RATE (ml/min)	CUMULATIVE VOL (GALLONS)	DISSOLVED OXYGEN (mg/L)	TEMP (C)	SPEC. COND (umhos)	pH	ORP (mV)	TURBIDITY (NTU)

SAMPLING ORDER			PRESERVATIVES		BOTTLES		SAMPLE NUMBER	TIME	CHECKED BY/ DATE
					COUNT/ VOLUME	TYPE			
1	VOC -CLP(Low Level) 8260B		4 deg. C	HCL	3/ 40 ml	VOA			
2	SVOC 8270C		4 deg. C		1 x 1L	Am G			
3	PESTICIDES 8081		4 deg. C		1 x 1L	Am G			
4	PCBs 8082				1 x 1L				
5	METALS 6010 & 7###		4 deg. C	HNO3	1 x 500 mL	HDPE			
6	CYANIDE 9012		4 deg. C	NaOH	1 x 500 mL	HDPE			
7	Total Pet Hydrocarbon		4 deg. C	HCl	1 x 1L	Am G			

COMMENTS: (QA/QC?)

IDW INFORMATION:

PAGE OF

SAMPLING RECORD - SURFACE SOIL/SEDIMENT

PARSONS | **CLIENT: USACOE** | **INSPECTOR :** | **DATE:**

PROJECT:
Plume Area:

SOIL TYPE
SURFACE SOIL SEDIMENT

COMMENTS:

MONITORING

INSTRUMENT	DETECTOR	READING

SAMPLE INFORMATION					SOIL INFORMATION					
LOCATION	SAMPLE NUMBER	SAMPLE DEPTH (in) TOP	SAMPLE DEPTH (in) BOTTOM	TIME (military)	GRAB or COMPOSITE SAMPLE	SAMPLE DESCRIPTION (Burmister method)	USCS Classification	VOC Screen (PPM)	QC Split (yes or no)	Other Notes

PAGE OF

SAMPLING RECORD - SOIL

Seneca Army Depot Activity	PARSONS	DATE:

CONSULTANT: _____
PROJECT: _____
LOCATION:

INSPECTOR: _____
LABORATORY: _____
SAMPLING STAFF: _____
CHAIN OF CUSTODY #: _____

WEATHER / FIELD CONDITIONS CHECKLIST (RECORD MAJOR CHANGES)

TIME (24 HR)	TEMP (APPRX)	WEATHER (GEN.)	REL. HUMIDITY (APPRX)	WIND VELOCITY (APPRX)	WIND DIRECTION (0 - 360)	GROUND / SITE SURFACE CONDITIONS	MONITORING INSTRUMENT	MONITORING DECTECTOR

LOC ID	SAMPLE #	DEPTH RANGE	DEPTH TIME	TYPE GRAB/COMP	COLOR	GRAIN SIZE	USCS CLASS	FOREIGN MAT. (Y/N)	SAMPLE DEVICE	CONTAINER SIZE/TYPE	MON. VOC/RAD	QC SPL (Y/N)

Note: Cleaning Procedure according to SOP.

PAGE OF

PAGE OF

SAMPLING RECORD - SURFACE WATER

SENECA ARMY DEPOT ACTIVITY	PARSONS	DATE:

CONSULTANT: _____
PROJECT: _____
LOCATION:

INSPECTOR: _____
LABORATORY: _____
LAB. STAFF: _____
CHAIN OF CUSTODY #: _____

WEATHER / FIELD CONDITIONS CHECKLIST (RECORD MAJOR CHANGES)

TIME (24 HR)	TEMP (APPRX)	WEATHER (GEN.)	REL. HUMIDITY (APPRX)	WIND (FROM) VELOCITY (APPRX)	WIND (FROM) DIRECTION (0 - 360)	GROUND / SITE SURFACE CONDITIONS	MONITORING INSTRUMENT	MONITORING DECTECTOR

LOC ID	SAMPLE #	DFS	DEPTH	TIME	TEMP	MON. VOC	MON. CLR	TURBIDITY (NTU)	pH	SPEC COND	D.O.	SAMPLING DEVICE	CONT TYPE / SIZE	QC SPL (Y/N)

DFS-DISTANCE FROM SHORE (FEET)
IDENTIFY UNITS FOR ALL MEASURMENTS
CLEANING PROCEDURES ACCORDING TO SOP

SAMPLING RECORD - SURFACE WATER

SENECA army DEPOT ACTIVITY	PARSONS	WELL #: MW

SAMPLING ORDER		TAL/ TCL	PRESERV.	BOTTLES		SAMPLE NO.	DATE/TIME		CHECKED BY/ DATE
				COUNT/ VOLUME	TYPE				
1	VOA/CLP			3/ 40 ml	G. vial				
1A	VOA/524.2			3/ 40 ml	G. vial				
2	SVOC			2/ 1 L	G. Amber				
3	HERB			2/ 1 L	G. Amber				
4	PEST/ PCB			2/ 1 L	G. Amber				
5	METALS + Sn			1/ 1 L	P				
6	CN			1/ 1 L	P				
7	TPH			2/ 1 L	G				
8	Hardness								
9	TDS								
10	COD								
11	SULFIDE			1/ 500 ml	G				
12	CATIONS K, Mn, Mg, Fe, Na			1/ 1 L	G. Amber				
13	ANIONS			1/ 1 L	P				
14	AMMONIA			1/ 1 L	P or G				
15	GROSS ALPHA/BETA			1/ 1 Gallon	P				

QA/QC **BOTTLE COUNTS ARE TRIPLED IF MS/ MSD SAMPLES ARE COLLECTED**

QA/QC DUPLICATE SAMPLE COLLECTED? YES NO

Duplicate Sample Name: _____

MRD Sample Name: _____

QA/QC rinsate sample name: _____

MATRIX SPIKE sample collected? YES NO

INVESTIGATION DERIVED WASTE (IDW):

DATE:				
VOLUME:				
DRUM #, LOCATION:				

COMMENTS:

INVESTIGATION DERIVED WASTE: DRUM INVENTORY
SENECA ARMY DEPOT, ROMULUS, NY

DRUM NUMBER (1),(2)	DRUM LOCATION	ORIGIN OF CONTENTS (3)	AMOUNT	DATE

NOTES:

1) Drum numbers should indicate the SEAD from which they come. For example, the first drum from SEAD-4 should be numbered 4-1.
2) Add an "S" for soil/sediment, and a "W" for water, i.e., 4-1W.
3) Specify the contents of the drum (boring #'s, well #'s, decon water, PPE, etc.).

Visitor Sign-In

Date	Name	Company	Time in	Time Out	Escorted By

SDG TRACKING FORM

Project: _____

SDG Open Date: _____ (Arrival date of first sample at the lab)
SDG Close Date: _____ (2 weeks or 20 samples)
SDG Matrix: _____
Lab SDG #: _____

	Samp ID	QC Code	Associated DU	Associated RB	Associated TB
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					

	Rinse Blank Sample Ids	Trip Blank Samp IDs
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		

QC Codes

SA = Sample
DU = Duplicate
MS = Matrix Spike
MSD = Matrix Spike Duplicate

Water Analysis Instrument Calibration Form

Project: Ash Landfill Biowall Pilot Test						
Date:	Time:	Make/Model:	Display S/N:		Cal By:	Cal By:
HACH DR 850					Morning	End of Day
Parameter:	Module Number:	Reagent	Standard Solution:	Accuracy Range;	Reading:	Reading:
Ferrous Iron	Method Number: 8146	Single Reagent Phenanthroline-Ferrover 10ml	50 mg/L standard solution (Ampoule) Dilute with 50ml of Di water to make a 1 mg/L solution	.99 - 1.10 mg/L		
Fe2+						
Range (0 to 3.00 mg/L)	Program # 33					
Manganese	Method Number: 8034	Two part reagent add Citrate Powder than Sodium Periodate to sample cell	Use 250mg/L standard Ampoule to mix 1ml of (250mg/L) standard with 50 ml of DI water to create a 5mg/L solution.	4.90 - 5.10mg/L		
Mn						
Range (0 to 20 mg/L)	Program # 41					
Hydrogen Sulfide	Method Number: 8131	Two part reagent add 1ml of reagent 1 and 1ml of reagent 2 to Di water and sample	Method Methyl Blue - 4500-S2-	NA		
H2S						
Range (0 to 0 .70 mg/L)	Program #-91					
	Time:	Make/Model:	Display S/N:		Cal By:	Cal By:
Digital Titration					Morning	End of Day
Parameter:	Reagent	Titration Cartridge	Standard Solution:	Accuracy Range;	Reading:	Reading:
Carbon Dioxide	Method Number: 8205	Sodium Hydroxide titration Cartridge 0.3636	Use 1 ml of 10,000 mg/L standard to titrated sample and record number of digits required.	NA		
Co2						
Range (0 to 200 mg/L)	Phenolphthaleine					
Alkalinity	Method Number: 8203	Sulfuric Acid Titration Cartridge 1.600	Use 1ml of 500mg/L solution added to titrated sample and record digits	NA		
Range (0 to 4000 mg/L as CaCo3)	Phenolphthaleine					

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PARSONS

Daily Operational Check Log
Instrument #_____

SOP-R.SUR-1-1 -_____ Page __ of ___
Revision 0
Last Date Calibrated: _____

Calibration Due Date: _____

Project Title: _____
Project Number: _____
Prepared By Print: _____
Prepared By Signature:_____ **Date:** _____
Verified By Signature: _____**Date:** _____

Meter Make/Model: _____
Meter Serial No.: _____
Detector Make/Model: _____
Detector Serial No.: _____

(optional data enter as needed)
Isotope: _____ **Efficiency:** _____
Isotope: _____ **Efficiency:** _____
Isotope: _____ **Efficiency:** _____
Isotope: _____ **Efficiency:** _____
Channel 1 Window: _____ **to** _____ **(keV)**
Channel 2 Window: _____ **to** _____ **(keV)**

Voltage Consistent With Calibration Certificate			No	Acceptable Background Range		Acceptable Source Check Range	

Date/ Time	Performed By (Print and initial)	Visual/ Battery Check	Background Check		Source Check			Channel (optional)	Remarks
			Gross Reading (___-minute Scalar)	Pass/ Fail	Gross Reading (cpm) (___-minute Scalar)	Source #	Pass/ Fail		

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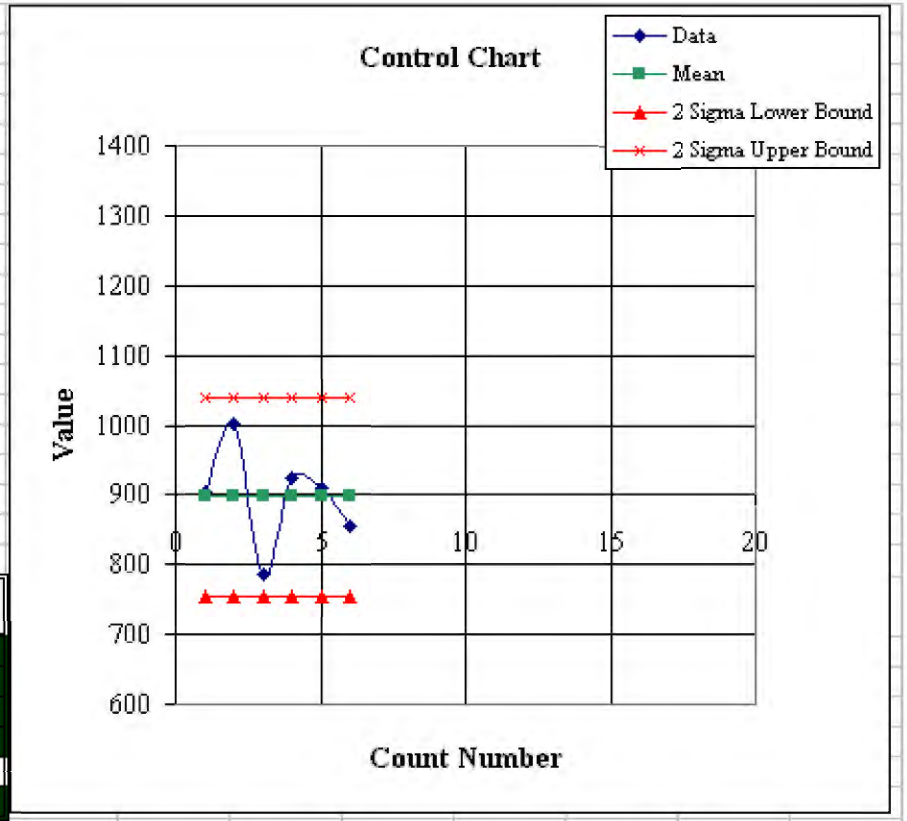
PARSONS **Daily Operational Check Log (Continuation Sheet)** **SOP-R.SUR-1-1 -_____ Page __ of ___**
Instrument #_____ **Revision 0**

Date/ Time	Performed By (Print and initial)	Visual/ Battery Check	Background Check		Source Check			Channel (optional)	Remarks
			Gross Reading (___) (___-minute Scalar)	Pass/ Fail	Gross Reading (___) (___-minute Scalar)	Source #	Pass/ Fail		

Example of a Control Chart

Parameter Being Tracked	Cs-137 0.661 MeV peak counts, post fine tuning	
Electectronics		
Instrument Type	URSA-MCA	
Model Number	Universal Radiation Spectrum Analyzer	
Manufacturer	RSA	
Serial Number	20291	
Detector		
Instrument Type	Fidler	
Model Number	M-23	
Manufacturer	Ortec	
Serial Number	X-111	
Geometry	Center Line Area Source at 4"	
ROI	Cs-137 0.661 MeV peak	
Count Data		
	Mean=	897.1667
	STDEV=	71.46025

Date/Time	Data Number	Data	Pull Block				Status
1/1/00 0:00	1	905	1	897.1667	754.2462	1040.087	OK
1/5/00 0:00	3	1001	2	897.1667	754.2462	1040.087	OK
1/6/00 0:00	4	787	3	897.1667	754.2462	1040.087	OK
1/7/00 0:00	5	923	4	897.1667	754.2462	1040.087	OK
1/10/00 0:00	6	911	5	897.1667	754.2462	1040.087	OK
1/2/00 0:00	2	856	6	897.1667	754.2462	1040.087	OK



.3

PARSONS

Surface Radiation
Field Measurement Datasheet

SOP-R-SUR-1-2- _____ **Revision 0**
Page ___ **of** ___ **Date**: _____

Project Title: _____

Project Number: _____

Building/area/Floor: _____

Room/Unit Designation: _____

Surveyor (print):_____ **Surveyor Signature**:_____ **Date**: _____

Verifier (print): _____ **Verifier Signature**: _____ **Date**: _____

Complete FS (print):_____ **FS Signature**: _____ **Date**: _____

Measurement Location		**Direct Surface Reading static Y/N)**			**Direct Surface Reading static (Y/N)**			**Alt. Distance (optional) _____cm (left instr)**
		Type _____ Count Time (M) _____			**Type _____ Count Time (M) _____**			**Alt. Distance (optional) _____cm (right instr)**
No	**Per Reference Map**	**Value (_____)**	**Channel (optional)**	**Instr. #**	**Value (_____)**	**Channel (optional)**	**Instr. #**	**Remarks**
Instr. Check Source								

Specialized Geometry (optional):

PARSONS	Personnel Contamination Datasheet	SOP-R-SUR-1-3 _____ Revision 0 Page 1 of 2 Date: _____

Individual' Name:		Employer		Employee #	
Individual's Address:		Permanent Work Location:			

No	Location (ref. Drawing attached)	Instrument	Activity	Activity Units	Instrument	Activity	Activity Units	Remarks/Comments

Instrumentment Data					Projected			
No	Manufacturer	Model	Seria	Attach	Lapsed Time for initial exposure		Basis:	
					Lapsed Time for residual exposure		Basis:	
					Decon Actions:			

Position	Name (Print)	Employer	No.	Permanent Work Location & phone #)	Signature	Date
Health and Safety						
Field Supervisor						
Health Physicist (if						
Surveyor						

PARSONS	Personnel Contamination Datasheet	SOP-R-SUR-1-3 _____ Revision 0 Page 2 of 2 Date: ____					
Analysis Health Physicist		**Employer**		**Phone**			
Analyst's Title		**Permanent Work Location:**					
Regulatory Basis for Analysis		**Analysis/Calculation of Dose Required**	**Yes**		**No**		

Dose Analysis (Reference applicable Parson's Calculation Procedure) (if required):

Projected Dose				**Explanation & Comments:**
Organ/Location	**Dose (mrem)**	**Dose (TEDE)**	**Total Effective**	

Position	**Name (Print)**	**Employer**	**No.**	**Permanent Work (& phone**	**Signature**	**Date**
Original Project Manager					**NA**	**NA**
Analyst						
Reviewer		NA	**NA**	**NA**		

Explosives Usage Record

Contract Number:

Team Number: Date: Project Name:

Team Leader: Work Areas & Grid Numbers:

Explosives Issued Signature Of Team Leader:

Item	Quantity	Lot Number	Checkers Initials

Explosives Expended Signature Of Team Leader

Item	Quantity	Lot Number	Checkers Initials

Explosives Returned Signature Of SUXOS:

Item	Quantity	Lot Number	Checkers Initials

The signatures in each section of this document indicate that the items listed in that section were in fact issued, expended, or returned to storage and that the quantities listed were verified through a physical count.

Magazine Data Card

Nomenclature:_____
Lot Number: Unit:_____ Date Of Issue:_____

Date	Name	Received	Issue	Balance	Checker's Initials

The signatures in each section of this document indicate that the items listed were in fact issued, expended, or returned to storage and that all quantities listed were verified through a physical count.

Explosive Vehicle Inspection, ON-SITE			
This form must be filled out prior to loading for any vehicle carrying explosives.			
This form is for use on site only; if traveling on public highways, use DD Form 626			
DRIVER'S NAME		LICENSE NUMBER	
COMPANY			
TYPE OF VEHICLE		VEHICLE NUMBER	
INSPECTION DATE/TIME		INSPECTOR	
PART INSPECTED	SAT.	UNSAT.	COMMENT
HORN			
STEERING SYSTEM			
WIPERS			
MIRRORS			
FIRE EXTINGUISHERS (10 ABC, 2 EACH)			
REFLECTORS			
EMERGENCY FLASHERS			
LIGHTS			
ELECTRIC WIRING			
FUEL SYSTEM			
EXHAUST SYSTEM			
BRAKE SYSTEM			
SUSPENSION			
CARGO SPACE			
TIRES, WHEELS, RIMS			
TAILGATE			
TARPAULIN			
INSPECTION RESULTS (INSPECTOR INITIAL)			
ACCEPTED:			
REJECTED:			
REMARKS			
DRIVER'S SIGNATURE/DATE			INSPECTOR'S SIGNATURE/DATE

DID OE-005-05.01
Attachment A

☐ QC checked by _____ Date: _____

Field Data Sheet

☐ QA checked by _____ Date: _____

Project Name: _____ **Project Location:** _____

Geophysical Contractor: _____ **Design Center POC:** _____

Project Geophysicist: _____ **Site Geophysicist:** _____

Survey Area ID: _____ **Date:** _____ **Field Team:** _____

Survey Type: ☐Grid ☐Meandering Path ☐Transect ☐Other _____

Coordinate System: ☐UTM ☐State Plane NAD _____ ☐Local ☐Other _____ **Unit of Measure:** ☐ meters ☐ feet

Sketch of Survey Area: **Approx. Scale:** _____ **North Arrow:**

_____

Terrain:
☐Level ☐Moderate Slope ☐Steep
☐Rolling ☐Ruts ☐Gullies
☐Rocky ☐Swampy ☐Dangerous

Tree Cover: **Tree Height:** ____
☐None ☐Light ☐Medium ☐Thick

Brush:
☐None ☐Light ☐Medium ☐Thick

Weather:
☐Sunny ☐Cloudy ☐Drizzle
☐Rain ☐Thunderstorms ☐Hail
☐Fog ☐Humid ☐Snow

Grid Corner Coordinates:

	UTM/State Plane	Local
SW	_____, _____	_____, _____
NW	_____, _____	_____, _____
NE	_____, _____	_____, _____
SE	_____, _____	_____, _____

	Start	End	File Name
Battery Voltage:	_____	_____	
Static Background Value:	_____	_____	_____, _____
Static Response Value:	_____	_____	_____, _____

Instrument Clock Drift: _____

Raw Data File Name: _____ **Repeat Data File Name:** _____

Geophysical Instrumentation: _____ **Serial Number:** _____

Base Station: _____ **Serial Number:** _____

Navigation Method: _____ **Serial Number:** _____

Additional Comments: _____

Geophysical Dig Sheet and Target History

Page ____ of _____

Reacquisition Geophysical Equipment Used	Component	Serial #	Grid Background Value (mV / nT)	Date	Time

Project Name: ___________________________________
Project Location: ___________________________________
Date: ___________________________________
Coordinate System: ___________________________________
Survey Area ID: ___________________________________
Sector: ________ Grid: ____________
Field Book ID: ___________________________________

Geophysical Contractor: ____
Project Geophysicist: ____
Site Geophysicist: ____
Field Team: ____
COE Design Center POC: ____
COE Project Engineer: ____
COE Geophysicist: ____

	Original Survey						Reacquisition Survey			Dig Results											Post-Dig UXO QC Results			Post-Dig Geophysical QC		
													Offset													
Unique Target ID	Easting Coord. (ft/m)	Northing Coord. (ft/m)	Channel ID (ie-C1 ….C4, top sensor, gradient, etc)	Response Amplitude (units*)	Dig Priority (0 is no dig-known anomaly source,1 is highest dig recommendation, etc..)	Date	Channel ID (ie-C1 or C4, top sensor, gradient)	Response Amplitude (units*)**	Date	Anomaly type ***	Approx. weight (lbs-oz / kg-g)	Comments	Distance (ft / m)	Direction (N, NE, etc.)	Orientation of Nose (Azimuth deg) **	Inclination of Nose (deg) **	Depth to Top of Item (in/cm)	Digital Photo Filename **	Date	Team Leader Initials	Excavation Hole Cleared?	UXO QC Spec. Initials	Date	Agreement between Dig Results & Geophysical Data? (G=good, P=poor, U=unacceptable)	Geophysicist QC Initials	Date

Note: *Fill in Acceptable Units (mV, nT/m, ppt, etc)
**Optional field – refer to SOW for applicability to specific project
For ***Anomaly type, use U for UXO, F for frag, OS for ordnance related scrap, S for scrap,
A for small arms ammunition, NC for no contact, O for other.

WIPE/CORE SAMPLING RECORD

SITE:	ANALYTE:
DATE/TIME:	SAMPLE MEDIA:
BUILDING NO.	SOLVENT:
SAMPLERS:	

SAMPLE ID NUMBER	SAMPLE LOCATION	SURFACE TYPE	DIMENSIONS OF SAMPLE AREA	TOTAL AREA

SKETCH AND GENERAL COMMENTS:

Table 2 (continued)
SW846 - Water

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Metals	6010, 7000 Series			
Antimony	"		$0.00	$0.00
Arsenic	"	6	$0.00	$0.00
Barium	"	5	$0.00	$0.00
Beryllium	"		$0.00	$0.00
Boron	"		$0.00	$0.00
Cadmium	"	5	$0.00	$0.00
Calcium	"		$0.00	$0.00
Hexavalent Chromium	"		$0.00	$0.00
Total Chromium	"	5	$0.00	$0.00
Cobalt	"		$0.00	$0.00
Copper	"	5	$0.00	$0.00
Iron	"		$0.00	$0.00
Lead	"	7	$0.00	$0.00
Magnesium	"		$0.00	$0.00
Mercury	"	7	$0.00	$0.00
Nickel	"		$0.00	$0.00
Potassium	"		$0.00	$0.00
Selenium	"	5	$0.00	$0.00
Silver	"		$0.00	$0.00
Sodium	"		$0.00	$0.00
Strontium	"		$0.00	$0.00
Thallium	"		$0.00	$0.00
Tin	"		$0.00	$0.00
Vanadium	"		$0.00	$0.00
Zinc	"	5	$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 06/2000

Table 3
SW846 - Soil/Sediment

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Volatile Organics	8010		$0.00	$0.00
Nonhalogenated Volatile Organics	8015		$0.00	$0.00
Volatile Aromatics	8020	1	$0.00	$0.00
Volatile Organics	8021		$0.00	$0.00
Phenolics	8040		$0.00	$0.00
Pesticides/PCBs	8081	183	$0.00	$0.00
Pesticides/PCBs (Dilutions only)	8081		$0.00	$0.00
Volatile Organics GC/MS	8260	67	$0.00	$0.00
B/N/As	8270	66	$0.00	$0.00
B/N/As (Dilution runs only)	8270		$0.00	$0.00
Polynuclear Aromatic Hydrocarbons	8100 or 8310	67	$0.00	$0.00
Organophosphorous Pesticides (Capillary Column)	8141	23	$0.00	$0.00
Chlorophenoxy Acid Herbicides	8150	36	$0.00	$0.00
17 Hazardous Metals - Sb, As, Ba, Be, Cd, Total Cr, Co, Cu, Pb, Hg, Ni, Se, Ag, Tl, Sn, V, Zn	6010, 7000 Series	34	$0.00	$0.00
Cyanide	9010	2	$0.00	$0.00
Sulfide	9030		$0.00	$0.00
pH	9040	2	$0.00	$0.00
Total Organic Halogen	9020		$0.00	$0.00
Total Organic Carbon	9060	136	$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 06/2000

Table 3 (continued)
SW846 - Soil/Sediment

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Corrosivity (pH only)	Section 2.1.1	13	$0.00	$0.00
Corrosivity (Nace)	Section 2.1.1		$0.00	$0.00
Ignitability	Section 2.1.2	4	$0.00	$0.00
Reactivity	Section 2.1.3	13	$0.00	$0.00
Extraction Procedure Toxicity (Extraction Only)	Section 2.1.4	11	$0.00	$0.00
Full Appendix IX (NYS Appendix 33) (not including Dioxin)			$0.00	$0.00
Toxicity Characteristic Leaching Procedure:				
Metals and Semivolatile Extract Preparation	See ASP	23	$0.00	$0.00
Zero Headspace Volatile Extract Preparation	See ASP	26	$0.00	$0.00
TCLP Metals - As, Ba, Cd, Total Cr, Pb, Hg, Se, Ag	See ASP	78	$0.00	$0.00
IR Scan	See ASP		$0.00	$0.00
Cleanups				
Alumina Cleanup	3610		$0.00	$0.00
Forisil Cleanup	3620		$0.00	$0.00
Silica Gel Cleanup	3630		$0.00	$0.00
Gel-Permeation Cleanup	3640		$0.00	$0.00
Acid-Base Partition Cleanup	3650		$0.00	$0.00
Sulfur Cleanup	3660		$0.00	$0.00
Sulfuric Acid Cleanup	3665A		$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 06/2000

Table 3 (continued)
SW846 - Soil/Sediment

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Metals	6010, 7000 Series			
Antimony	"		$0.00	$0.00
Arsenic	"	104	$0.00	$0.00
Barium	"	4	$0.00	$0.00
Beryllium	"		$0.00	$0.00
Boron	"		$0.00	$0.00
Cadmium	"	131	$0.00	$0.00
Calcium	"		$0.00	$0.00
Hexavalent Chromium	"		$0.00	$0.00
Total Chromium	"	77	$0.00	$0.00
Cobalt	"		$0.00	$0.00
Copper	"	104	$0.00	$0.00
Iron	"	73	$0.00	$0.00
Lead	"	104	$0.00	$0.00
Magnesium	"		$0.00	$0.00
Mercury	"	65	$0.00	$0.00
Nickel	"	100	$0.00	$0.00
Potassium	"		$0.00	$0.00
Selenium	"	101	$0.00	$0.00
Silver	"	27	$0.00	$0.00
Sodium	"		$0.00	$0.00
Strontium	"		$0.00	$0.00
Thallium	"		$0.00	$0.00
Tin	"		$0.00	$0.00
Vanadium	"		$0.00	$0.00
Zinc	"	31	$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 06/2000

Table 4
SW846 - Hazardous Wastes

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Volatile Organics	8010		$0.00	$0.00
Nonhalogenated Volatile Organics	8015		$0.00	$0.00
Volatile Aromatics	8020		$0.00	$0.00
Volatile Organics	8021		$0.00	$0.00
Phenolics	8040	2	$0.00	$0.00
Pesticides/PCBs	8080		$0.00	$0.00
Pesticides/PCBs (Dilutions only)	8080		$0.00	$0.00
Pesticides/PCBs	8081	81	$0.00	$0.00
Pesticides/PCBs (Dilutions only)	8081		$0.00	$0.00
Volatile Organics GC/MS	8260	109	$0.00	$0.00
B/N/As	8270	37	$0.00	$0.00
B/N/As (Dilution runs only)	8270		$0.00	$0.00
Polynuclear Aromatic Hydrocarbons	8100 or 8310		$0.00	$0.00
Organophosphorous Pesticides (Capillary Column)	8141	2	$0.00	$0.00
Chlorophenoxy Acid Herbicides	8150	8	$0.00	$0.00
17 Hazardous Metals - Sb, As, Ba, Be, Cd, Total Cr, Co, Cu, Pb, Hg, Ni, Se, Ag, Tl, Sn, V, Zn	6010, 7000 Series	79	$0.00	$0.00
Cyanide	9010	5	$0.00	$0.00
Sulfide	9030		$0.00	$0.00
pH	9040	38	$0.00	$0.00
Total Organic Halogen	9020		$0.00	$0.00
Total Organic Carbon	9060		$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 10/95

Table 4 (continued)
SW846 - Hazardous Wastes

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Corrosivity (pH only)	Section 2.1.1	18	$0.00	$0.00
Corrosivity (Nace)	Section 2.1.1		$0.00	$0.00
Ignitability	Section 2.1.2	89	$0.00	$0.00
Reactivity	Section 2.1.3	4	$0.00	$0.00
Extraction Procedure Toxicity (Extraction Only)	Section 2.1.4		$0.00	$0.00
Full Appendix IX (NYS Appendix 33) (not including Dioxin)			$0.00	$0.00
Toxicity Characteristic Leaching Procedure:				
Metals and Semivolatile Extract Preparation	See ASP	5	$0.00	$0.00
Zero Headspace Volatile Extract Preparation	See ASP	2	$0.00	$0.00
TCLP Metals - As, Ba, Cd, Total Cr, Pb, Hg, Se, Ag	See ASP	2	$0.00	$0.00
IR Scan	See ASP		$0.00	$0.00
Cleanups				
Alumina Cleanup	3610		$0.00	$0.00
Forisil Cleanup	3620		$0.00	$0.00
Silica Gel Cleanup	3630		$0.00	$0.00
Gel-Permeation Cleanup	3640		$0.00	$0.00
Acid-Base Partition Cleanup	3650		$0.00	$0.00
Sulfur Cleanup	3660		$0.00	$0.00
Sulfuric Acid Cleanup	3665A		$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 06/2000

Table 4 (continued)
SW846 -Hazardous Waste

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Metals	6010, 7000 Series			
Antimony	"		$0.00	$0.00
Arsenic	"		$0.00	$0.00
Barium	"		$0.00	$0.00
Beryllium	"		$0.00	$0.00
Boron	"		$0.00	$0.00
Cadmium	"	69	$0.00	$0.00
Calcium	"		$0.00	$0.00
Hexavalent Chromium	"		$0.00	$0.00
Total Chromium	"	69	$0.00	$0.00
Cobalt	"		$0.00	$0.00
Copper	"		$0.00	$0.00
Iron	"	2	$0.00	$0.00
Lead	"	72	$0.00	$0.00
Magnesium	"		$0.00	$0.00
Mercury	"	69	$0.00	$0.00
Nickel	"		$0.00	$0.00
Potassium	"		$0.00	$0.00
Selenium	"		$0.00	$0.00
Silver	"		$0.00	$0.00
Sodium	"		$0.00	$0.00
Strontium	"		$0.00	$0.00
Thallium	"		$0.00	$0.00
Tin	"		$0.00	$0.00
Vanadium	"		$0.00	$0.00
Zinc	"		$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 10/95

Table 5
Special Methods

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Organics Screen (Water Only)	503.1	6	$0.00	$0.00
Purgeable Organics (Water Only)	524.2	4	$0.00	$0.00
Extractable Organics (Water Only)	525		$0.00	$0.00
Steam Distillation for Highly Chlorinated Organics and PCBs (Soils Only)	See ASP		$0.00	$0.00
Total Petroleum Hydrocarbons	418.1	35	$0.00	$0.00
Total Petroleum Hydrocarbons	8440		$0.00	$0.00
Methanol/Ethanol	See ASP	5	$0.00	$0.00
PCBs in Oil	8080		$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 10/95

Table 6
Superfund CLP - Special Methods

Parameter	Method*	Usage Factor	Cost per Sample Superfund Category Reporting Water
CLP-TCL Inorganics (Metals)	EPA SOW ILM04.0	110	$0.00
CLP-TCL Inorganics (Cyanide)	EPA SOW ILM04.0	37	$0.00
CLP-TCL Purgeable Organics	EPA SOW OLM04.2	244	$0.00
CLP-TCL Semivolatile Organics	EPA SOW OLM04.2	107	$0.00
CLP-TCL Semivolatile Organics (Dilution runs only)	EPA SOW OLM04.2		$0.00
CLP-TCL Pesticides/PCBs	EPA SOW OLM04.2	42	$0.00
CLP-TCL Pesticides/PCBs (Dilution runs only)	EPA SOW OLM04.2		$0.00
CLP-TCL PCBs only	EPA SOW OLM04.2		$0.00
CLP-TCL Low Concentration Purgeable Organics	EPA SOW OLC02.1		$0.00
CLP-TCL Low Concentration Semivolatile Organics	EPA SOW OLC02.1		$0.00
CLP-TCL Low Concentration Pesticides/PCBs	EPA SOW OLC02.1		$0.00

Parameter	Method*	Usage Factor	Cost per Sample Superfund Category Reporting Soil/Sediment
CLP-TCL Inorganics (Metals)	EPA SOW ILM04.0	126	$0.00
CLP-TCL Inorganics (Cyanide)	EPA SOW ILM04.0	47	$0.00
CLP-TCL Purgeable Organics	EPA SOW OLM04.2	109	$0.00
CLP-TCL Semivolatile Organics	EPA SOW OLM04.2	91	$0.00
CLP-TCL Semivolatile Organics (Dilution runs only)	EPA SOW OLM04.2		$0.00
CLP-TCL Pesticides/PCBs	EPA SOW OLM04.2	94	$0.00
CLP-TCL Pesticides/PCBs (Dilution runs only)	EPA SOW OLM04.2		$0.00
CLP-TCL PCBs only	EPA SOW OLM04.2		$0.00
CLP-TCL Low Concentration Purgeable Organics	EPA SOW OLC02.1		$0.00
CLP-TCL Low Concentration Semivolatile Organics	EPA SOW OLC02.1		$0.00
CLP-TCL Low Concentration Pesticides/PCBs	EPA SOW OLC02.1		$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 10/95

Table 6 (continued)
Superfund CLP - Special Methods

Parameter	Method*	Usage Factor	Cost Per Sample Superfund Category Reporting Water
Metals			
Aluminum	EPA SOW ILM04.0		$0.00
Antimony	“		$0.00
Arsenic	“		$0.00
Barium	“	6	$0.00
Beryllium	“		$0.00
Cadmium	“	6	$0.00
Total Chromium	“	18	$0.00
Cobalt	“		$0.00
Copper	“		$0.00
Iron	“	18	$0.00
Lead	“	2	$0.00
Magnesium	“	17	$0.00
Manganese	“	16	$0.00
Mercury	“	16	$0.00
Nickel	“		$0.00
Potassium	“	17	$0.00
Selenium	“		$0.00
Silver	“		$0.00
Sodium	“	17	$0.00
Thallium	“		$0.00
Vanadium	“		$0.00
Zinc	“		$0.00
Cyanide	“		$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 10/95

Table 6 (continued)
Superfund CLP - Special Methods

Parameter	Method*	Usage Factor	Cost Per Sample Superfund Category Reporting Soil/Sediment
Metals			
Aluminum	EPA SOW ILM04.0		$0.00
Antimony	"		$0.00
Arsenic	"	40	$0.00
Barium	"		$0.00
Beryllium	"		$0.00
Cadmium	"	8	$0.00
Total Chromium	"	33	$0.00
Cobalt	"		$0.00
Copper	"		$0.00
Iron	"		$0.00
Lead	"	101	$0.00
Magnesium	"		$0.00
Manganese	"		$0.00
Mercury	"	24	$0.00
Nickel	"		$0.00
Potassium	"		$0.00
Selenium	"		$0.00
Silver	"		$0.00
Sodium	"		$0.00
Thallium	"		$0.00
Vanadium	"		$0.00
Zinc	"		$0.00
Cyanide	"		$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 10/95

Table 7
Special Services

Expert Witness Services		$0.00	per unit time
Quick Turnaround Service			
24 Hour Turnaround		1	times Cost
48 Hour Turnaround		1	times Cost
7 Day Turnaround		1	times Cost
14 Day Turnaround		1	times Cost
Extended Sample Storage		$0.00	/Sample/Day

Sample Containers (Price/Each)*	Usage Factor	Price per Container
Purgeables (Water)	714	$0.00
Purgeables (Soil/Sediment)	286	$0.00
Organic Extractables (Water)	792	$0.00
Organic Extractables (Soil/Sediment)	718	$0.00
Metals (Water)	383	$0.00
Metals (Soil/Sediment)	623	$0.00
Cyanides (Water)	105	$0.00
Cyanides (Soil/Sediment)	54	$0.00
Conventionals (Water)	1704	$0.00
Conventionals (Soil/Sediments)	278	$0.00

* Prices must be supplied, since containers obtained from one laboratory may not always be returned to that laboratory.

Table 8
Optional Special Methods

Parameter	Method*	Usage Factor	Cost Per Sample Category A Reporting	Cost Per Sample Category B Reporting
Oil Characterization				
Total Halogens	ASTM D1317		$0.00	$0.00
BTU (value/lb.)	ASTM D240		$0.00	$0.00
Sulfur Content	ASTM D129, D1552, D622			
Disposal Characteristics				
Water Content	ASTM E203		$0.00	$0.00
Density	ASTM E213		$0.00	$0.00
Color	USEPA 110		$0.00	$0.00
Cyanide	USEPA 9010		$0.00	$0.00
Alkalinity	USEPA 403		$0.00	$0.00

PCBs and Dioxins		Catagory B Reporting Only Water	Soil/Sediment
2,3,7,8-TCDD	1613	$0.00	$0.00
Chlorinated Dioxins and Dibenzofurans	8280	$0.00	$0.00
Chlorinated Dioxins and Dibenzofurans (HRMS)	8290	$0.00	$0.00
Congener PCB Analysis	1668A	$0.00	$0.00
Total Glycols	ASP 89-9	$0.00	$0.00

* Reporting requirements in accordance with New York State Department of Environmental Conservation Analytical Services Protocol (ASP), as revised 10/95

Appendix D

Minimum Specifications and Requirement for Electronic Data Deliverables

Appendix D

Parsons, Boston Massachusetts
Minimum Specifications and Requirements for Electronic Data Deliverables
Analytical Laboratory Data
(Updated October 26, 2005)

The following document identifies and defines Contractor's preferred specifications and requirements for electronic data reports that are produced by analytical laboratories working as a Subcontractor to Parsons Infrastructure and Technology (Parsons) in Boston Massachusetts. Potential Subcontractors are urged to closely review these specifications and requirements and provide Parsons (Contractor) with comments regarding potential changes that may be necessary due to differences in Subcontractor's capabilities and in-house systems and techniques in advance of the performance of analytical support services. If Contractor awards a subcontract for performance and completion of contract analytical services and the reporting of data resulting from the provision of such services, Contractor will expect Subcontractor to identify an acceptable electronic data reporting format for use throughout the duration of the subcontract. Prior to Subcontractor's transmission of an electronic data report, Contractor must provide Subcontractor with written approval of the Subcontractor's proposed electronic data reporting format. Once approved, the identified electronic data report format must be used for the transmittal of all electronic data reports to the Contractor under the subcontract. Deviation from the approved format that results in Contractor data entry delays or data loading errors for the data reported by Subcontractor may result in Contractor's rejection of data reports, withholding of partial or full payment for services pending transmittal of an acceptable electronic data report, and possible termination of the subcontract.

General Requirements

Electronic files must be readable by IBM-Compatible Personal Computers. A cover letter must be provided by Subcontractor that names and identifies the contents of all electronic data files that are being provided as part of an electronic data report. The Subcontractor's cover letter must also provide information identifying how the electronic files were generated by the laboratory (e.g., streaming electronic read directly from instrumentation, manually doubled keyed and cross checked by Subcontractor personnel or agents, etc.), how Subcontractor completed quality assurance and quality control of the electronic files to assure that the electronic data transmittal matched provided hard-copy results, and who to contact in the event deviations or problems are noted or encountered by Contractor.

Data Quality Control

The data submitted electronically must be identical in content (for the parameters identified in this document) to the data submitted on final hard copy deliverables.

Data Format Requirements

All analytical electronic data submissions will be reported in files that are readable by IBM compatible personal computers. ASCII formatted files or files readable by Excel, Lotus 1*2*3*, Access, dBase, or Oracle are acceptable. The files may be transmitted electronically via telecommunications, via the Internet, via disk, or via CD to Contractor's computer system. The Contractor must be notified and approve in writing of the Subcontractor's electronic transmission format prior to the collection of field samples. All subsequent data transmittals completed under the proposed scope of services must be made using the same format, unless the Contractor approves in writing of a change. The Subcontractor is responsible for contacting the Contractor and gaining approval of a revised format if such need arises during the course of the work. Any data submission provided that is not in an approved format or which does not load due to lack of required data or misplaced fields or delimiters will be returned to the Subcontractor for resubmission.

If the file is in ASCII format, it must be in either a fixed field format (i.e., the starting and ending column for each value is defined and constant for each record), or in delimited file format (i.e., a format where values are separated by a particular character- usually, a comma and character values are surrounded by double quotes). Each record will be contained on one line.

Data Compression

Electronic data files may be compressed to save space and time as long as the files are self-extracting or the decompression program is available to the Contractor without any cost. If a decompression routine is necessary, details of the program and where it may be obtained must be identified to the Contractor in Subcontractor's response to this request for cost quotation.

Data Content Requirements

Subcontractor must provide Contractor with a written description of the electronic data format that will be used for reporting all data resulting from the analysis of samples. The format of all data fields provided in the Subcontractor's electronic format must be described as either numeric, alphanumeric, date, logical, etc., and the length of each field or the field separation character (e.g., ",", <TAB>, <CR>, etc.) must be clearly defined. The order that data fields will be reported must be indicated. Once approved by the Contractor, the data reporting format must not change for the duration of the contract work.

All electronic submission packages must include a separate data file that provides the following sample description information for each distinct analytical method performed on a sample:

- Contractor Sample Identifier (Reproduced exactly as provided on the Chain-of-Custody provided by Contractor)
- Analysis Method
- Laboratory Sample Delivery Group (SDG) Identifier

- Laboratory Sampler Identifier
- Laboratory Identifier
- Date the Sample Was Received at Laboratory
- Date the Sample Was Extracted For Analysis
- Date the Sample Was Analyzed
- Sample Dilution Factor
- Sample Percent Moisture (for non-liquid samples)
- Laboratory Analysis Identifier (i.e., a lab defined identifier for an analysis that uniquely identifies a single run for a single aliquot)

All electronic submission packages must also include a separate electronic file that provides the following analytical result data for each parameter measured during an analysis:

- Contractor Sample Identifier (Reproduced exactly as provided on the Chain of Custody provided from the field)
- Laboratory Analysis Method Designation
- Contractor Sample Type Code (SA – sample, DU – duplicate, FB – field blank, TB – trip blank, etc.)
- CAS Number for the Parameter/Analyte Measured
- Laboratory Parameter/Analyte Name
- Result of Analytical Measurement for a Sample and Parameter
- Reporting Limit for this Analysis on This Parameter
- Reporting Limit Type (see **Table 1**)
- Unit Used for Reporting Results and Reporting Limits
- Result Qualifier(s)
- Result Qualifier(s) Decription (see **Table 2**)
- Laboratory Sample Identification Number
- Laboratory Sample Delivery Group Designation
- Handling Method
- Handling Date
- Handling Batch
- Handling Type (see **Table 3**)
- Analysis Group (see **Attachment 1**)
- Analysis Type (See **Table 4**)
- Laboratory Analysis ID
- Analysis Batch
- Analysis Date
- Run Batch
- Preparation Batch
- Preparation Method
- Preparation Date
- Cleaned Up Date

- Cleanup Batch
- Result Basis (Dry or Wet)

Additional data fields the laboratory would like to report may be appended to the above listed data items. However, all additional data fields provided by the laboratory must be identified to, and approved in writing by, the Contractor prior to the initiation of the field sample collection effort.

Contractor's sample identifier is a key field in several tables of the Contractor's database. It must be reported exactly as it was received at the Subcontractor's facility. All numbers, characters, capitalization, and punctuation must be maintained and no additional characters or spaces may be added to the Contractor's sample identifier. The Contractor sample identifier must be reported consistently. If, for example, the sample identifier will be the first word in the sample description field, it must always be reported as the first word in the sample description field.

CAS Number is a key field in several of the Contractor's database tables. Contractor's database preferentially uses CAS Numbers from which hyphens have been removed; however, Contractor has developed procedures for removing embedded hyphens from all files provided in one of the identified preferred electronic formats. Subcontractor must provide CAS Numbers for all analytes or compounds identified by the Chemical Abstracts Services. CAS Numbers are not required for analytes/parameters not listed by Chemical Abstract Services. If CAS Numbers are not available for a parameter/analyte, Subcontractor will leave the electronic CAS Number field empty within the electronic data report.

Contractor has developed a "preferred list of CAS Numbers that are used to identify analytes and compounds in the Contractor database. This preferred list is presented in **Tables 6-A** through **6-N** in the Seneca Generic Sampling and Analysis Plan (SAP). Contractor expects that all results reported electronically by Subcontractor will be reported using Contractor's preferred CAS Numbers that are listed in **Tables 6-A** through **6-N**. Deviation from the preferred list is allowed, but Subcontractor must identify deviations to the Contractor prior to the initiation of the field collection effort.

For analytical determinations for which tentatively identified compounds (TICs) are routinely reported (e.g., volatile and semivolatile organic compounds), Subcontractor shall provide a unique electronic data field that allows Contractor to rapidly identify and segregate TICs from normally reported compounds. The location of the unique data field for TICs must be pre-defined by Subcontractor in the electronic file format submitted to Contractor for approval prior to the performance of the field effort. Once approved the electronic report format for data containing TICs must remain constant.

All date fields must include the day, month and year. Contractor's preferred format is MM/DD/YYYY. If date field information is not available for individual records that are being reported electronically, the date field must be left blank and not be filled with space holder characters (e.g., ---, ***, ###). Subcontractor date field information must be consistent once it has been approved.

Contractor's database uses separate numeric fields to house analytical results and reporting limit data. Furthermore a separate alphanumeric field is used to house data qualifiers. Analytical results and reporting limit information shall not be provided as alphanumeric fields (e.g., > 5, less than 15) or as alphabetic fields (e.g., "ND", "NA"). Analytical results and reporting limits shall be standard numbers expressed in the correct number of significant figures. If data are unknown for either field, no value will be included in the field. A zero (0) is unacceptable for an unknown value or reporting limit. If a compound or analyte is not detected in a particular sample, it shall be reported as a null field; the reporting limit field shall be filled with the numeric reporting limit data (e.g., 5); the reporting limit type field shall be filled with the appropriate comment (see **Table 1**); the data qualifier field shall be filled with the appropriate data qualifier (e.g., "<", "U"); and the data qualifier description field shall be filled with the appropriate code number (see **Table 2**). If a compound is detected, the analytical result field shall contain only a valid number (e.g., 425), the reporting limit field shall contain a valid number (e.g., 330), the reporting limit type field (see **Table 1**), the qualifier field, and data qualifier description field shall be filled with the appropriate code (see **Table 2**). A null entry, indicating that a compound was detected without qualification, is a valid qualifier for analytical results reported by Subcontractor.

Accompanying Documentation

All electronic data submissions will include a hard copy report that includes the following file content information:

- Type of File Being Transmitted
- Format of File Being Transmitted
- Type of Submittal; Original, Full Replacement, or Correction
- Date of Transmission, Organization, Contact and Phone
- All File Names and File Sizes in Bytes Included in Data Transmission
- List of SDGs or Partial SDGs included in Each File
- Total Number of Samples Included in Each File
- Total Number of Records Included in Each File
- List of All Samples Included in Each File and Number of Results Reported for Each Sample

Analysis Group

Element Description

Links several analyses used to compute results for one method.

Data Type and Characteristics

VarChar2(30)

IRDMIS Equivalent: N/A

Element Is Used in the Following Upload File and ERIS Database

ERIS Upload File		ERIS Database	
Record	Column(s)	DB Table(s)	DB Column
ANALGRP	ANALYSIS_GROUP	ANALYSIS_GROUP	ANALY_GRP

Acceptable Entries

ASCII Character Set

Example of Analysis Group and related Analysis Method

Analysis_Group=Purgeables
CLIENT_METHOD_ID=PURGEABLES SW-846 8260

Table 1 - List of Reporting Limt Type

Below is a list of the Reporting Limit Type that are to accompany reported results. The laboratory must review the list of Reporting Limit Types and select the comment that best describes how the Reporting Limit was determined for an analysis.

Report Limit Type
ANSI/N42.23 Standard
Contract Required Detection Limit
IRDMIS Legacy Data
Method Defined Detection Limit
Instrument Detection Limit
Lowest Level of Detection
Minimum Detectable Activity
Method Detection Limit
Project Specific

Table 2 - List of Result Qualifer Description

Below is a list of Result Qualifier Descriptions that are to accompany reported results. The laboratory is to review the list of Result Qualifier Descriptions and must choose the appropriate Code for EACH laboratory qualifer that is reported.

Result Qualifier Description	Code
A non-SPCC or non-CCC compound in CCV exceeds 20% difference (% D) from the initial calibration curve.	LQD-01
Analysis is unconfirmed.	LQD-02
Analysis was confirmed.	LQD-03
Analyte concentration detected at a value between MDL and PQL.	LQD-04
Analyte concentration is above the upper reporting level.	LQD-05
Analyte detected in daily blank.	LQD-06
Amount detected is less than the Lower Calibration Limit.	LQD-07
Analyte found in blank as well as sample.	LQD-08
Analyte found in equipment blank as well as sample	LQD-09
Analyte found in field blank as well as sample	LQD-10
Analyte found in rinse blank as well as sample.	LQD-11
Analyte found in trip blank as well as in sample.	LQD-12
Analyte has saturated the detector.	LQD-13
Analyte quantitated on the secondary column.	LQD-14
Analyte recovery outside of certified range but within acceptable limits.	LQD-15
Analyte required for reporting purposes but not currently certified.	LQD-16
Analyzed for but not detected.	LQD-17
CCV recovery was above method acceptance limits. This target analyte was detected in the sample, but the sample was not reanalyzed.	LQD-18
CCV recovery was above method acceptance limits. This target analyte was detected in the sample, but the sample was not reanalyzed.	LQD-19
Co-elution	LQD-20
Concentration estimated. Analyte exceeded calibration range, Sample no longer available for reanalysis.	LQD-21
Coumpound does not meet correlation coefficient requirements in the calibration curve.	LQD-22
Data is rejected.	LQD-23
Did not meet QC criteria.	LQD-24
Duplicate (high) spike analysis not within control limits.	LQD-25
Duplicate analysis not within control limits.	LQD-26
Duplicate sample or Test Name.	LQD-27
Element run with background correction.	LQD-28
Elevated because of matrix interference, dilution required.	LQD-29
Ending calibration not within acceptable limits.	LQD-30
Equal to	LQD-31
Estimated concentration, below limit of quantitation.	LQD-32
Estimated concentration due to interference.	LQD-33
Estimated maximum possible concentration.	LQD-34
Greater than	LQD-35
High-spike recoveries excessively different.	LQD-36
Indicates the value is determined by the method of standard addition	LQD-37
Interferences in sample make quantitation and/or identification suspect.	LQD-38
Internal standard(s) not within acceptable limits.	LQD-39
Low spike recovery is not within control limits.	LQD-40
Low-spike recoveries excessively different.	LQD-41
Matrix spike recovery is high, the method control sample recovery was acceptable.	LQD-42
Missed holding time for extraction and preparation	LQD-43
Missed holding time for sample analysis.	LQD-44
Missed holding time; acceptable based holding-time study.	LQD-45
Missing Control Charts.	LQD-46
NOT DETECTED (SUBSTANTIALLY ABOVE THE REPORTED IN LABORATORY OR FIELD BLANKS)	LQD-47
Non-demonstrated/validated method performed for USAEC.	LQD-48
Non-target compound analyzed for and detected (GC/MS methods).	LQD-49
Non-target compound analyzed for and detected (non-GC/MS methods).	LQD-50
Non-target compound analyzed for but not detected (GC/MS methods).	LQD-51
Non-target compound analyzed for but not detected (non-GC/MS methods).	LQD-52
Not detected	LQD-53
Out of control but data accepted due to high recoveries.	LQD-54
Out of control, data rejected due to low recoveries.	LQD-55
Outside of QC limits.	LQD-56
Percent difference between 2 columns exceed.	LQD-57
Poor resolution.	LQD-58

Table 2 - List of Result Qualifer Description

Below is a list of Result Qualifier Descriptions that are to accompany reported results. The laboratory is to review the list of Result Qualifier Descriptions and must choose the appropriate Code for EACH laboratory qualifer that is reported.

Result Qualifier Description	Code
Quantitative interference in the sample.	LQD-59
Recovery is high in MS/MSD and in method control sample(s).	LQD-60
Recovery is low in MS/MSD and in method control sample(s).	LQD-61
Recovery not within control limits.	LQD-62
Reported results are affected by interferences or high background.	LQD-63
Result is below the PQL.	LQD-64
Result is biased high.	LQD-65
Result is biased low.	LQD-66
Result is from a dilution.	LQD-67
Results based on internal standard	LQD-68
Results less than CRL but greater than COD.	LQD-69
Results less than reporting limit but greater than instrument detection limit.	LQD-70
Sample filtered before analysis.	LQD-71
Sample interferences obscure peak of interest.	LQD-72
Sample subjected to unusual storage/preservation conditions.	LQD-73
Samples appear to have been extracted with hexane rather than methylene chloride. The hexane solvent peak interferes with the recovery of GRO (gasoline range organics).	LQD-74
Single analyte required from a multi-analyte method.	LQD-75
Spiked sample recovery not within control limits.	LQD-76
Tentatively identified compound (match greater than 70%).	LQD-77
Tentatively identified compound (match less than 70%).	LQD-78
The accuracy of the spike recovery value is reduced since the analyte concentration in the sample is disproportionate to spike level.	LQD-79
The associated blank spike recovery was above laboratory acceptance limits.	LQD-80
The associated blank spike recovery was below laboratory acceptance limits. Recovery was acceptable in MS/MSD.	LQD-81
The element was analyzed for, but not detected. The sample quantitation limit is an estimate due to variance from quality control limits.	LQD-82
The high-spike recovery is high.	LQD-83
The high-spike recovery is low.	LQD-84
The low-spike recovery is high.	LQD-85
The low-spike recovery is low.	LQD-86
Trace	LQD-87
Unknown	LQD-88
Value is estimated.	LQD-89
Variability in LCS/LCSD.	LQD-90

Table 3 - List of Handling Types

Below is a list of Handling Types that are to accompany reported results. The laboratory must review the list of Handling Types and must choose the appropriate Handling Type for EACH analysis method that is reported.

Handling Type
Air Dried
Ashed
Centrifuged
Decanted
Distilled
Dried
Filtered
Grind
Homogenized
Leached

Table 4 - List of Analysis Types

Below is a list of Analysis Types that are to accompany reported results. The laboratory must review the list of Analysis Types and must choose the appropriate Analysis Type for EACH analysis method that is reported.

Analysis Type
IRDMIS Legacy 00 - Special Test Names (no approval required)
IRDMIS Legacy 1A - Class 1A (GC/MS methods)
IRDMIS Legacy 1B - Class 1B (low sample throughput - not GC/MS)
IRDMIS Legacy 1M - Class 1M (GC/MS for volatiles & semivolatiles)
IRDMIS Legacy 1P - Class 1P (GC methods for pesticides & PCBs)
IRDMIS Legacy 99 - Special USAEC authorized (Data Qual "R" replaced)
IRDMIS Legacy C1 - Class 1 (quantitative)
IRDMIS Legacy C2 - Class 2 (quantitative)
IRDMIS Legacy NT - Non-AEC Approved Method (no approval required)
First Column Result: The Value Obtained from the First Column
Second Column Result: The Value Obtained from the Second Column
Confirmation Result. The confirmation result for a parameter.
First dilution of the original sample
Second dilution of the original sample
Third dilution of the original sample
Method of standard additions
Primary Result: The Primary Result for a Parameter
First reanalysis of a sample
Second reanalysis of a sample
Third reanalysis of a sample
System monitoring compound

Appendix E

Project Personnel Sign-Off Sheet

Appendix E
Project Personnel Sign-Off Sheet Template

Project Personnel	Title	Telephone Number	Signature	Date SAP Read
Todd Heino	Project Manager	(617)-449-1405		
Jeff Adams	Task Order Manager	(617)-449-1570		
Jackie Travers	Task Order Manager	(617)-449-1566		
James Lowerre	Quality Assurance Officer	(617)-449-1559		
Tom Andrews	Field Team Leader	(716) 633-7074		
Katherine LaPierre	Project Chemist	(512) 719-6000x6806		
David Miller	STL Pittsburgh, Project Manger	(412)963-7058		
Tony Bogolin	STL Buffalo, Project Manager	(716) 691-2600		
Cheryl Jones/Nancy Mattern	GEL, Charlestown, SC, Project Manger	(843) 556-8171		
Mike Perry/Mark Wilson	CAS, Rochester, NY, Project Manger	(585)288-5380		
TBD	Subcontractor project manager			

All the above identified personnel or any other key project personnel should read the appropriate sections of the approved SAP and perform the tasks as described. The signed sheets should be forwarded to Kaaren Godin at 150 Federal Street, Boston, MA 02110 (email: kaaren.godin@parsons.com) for the central project file.

Appendix F

Analytical Methods and Standard Operating Procedures

1. USEPA Region 2 Ground Water Sampling Procedure, Low Stress (Low Flow) Purging and Sampling

2. NIOSH Method 6009 – Mercury

3. NIOSH Method 7082 – Lead by Flame AAS

4. USEPA Region 1 Draft Standard Operating Procedure for Sampling Concrete in the Field

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION II

GROUND WATER SAMPLING PROCEDURE
LOW STRESS (Low Flow) PURGING AND SAMPLING

I. SCOPE & APPLICATION

This Low Stress (or Low-Flow) Purging and Sampling Procedure is the EPA Region II standard method for collecting low stress (low flow) ground water samples from monitoring wells. Low stress Purging and Sampling results in collection of ground water samples from monitoring wells that are representative of ground water conditions in the geological formation. This is accomplished by minimizing stress on the geological formation and minimizing disturbance of sediment that has collected in the well. The procedure applies to monitoring wells that have an inner casing with a diameter of 2.0 inches or greater, and maximum screened intervals of ten feet unless multiple intervals are sampled. The procedure is appropriate for collection of ground water samples that will be analyzed for volatile and semi-volatile organic compounds (VOCs and SVOCs), pesticides, polychlorinated biphenyls (PCBs), metals, and microbiological and other contaminants in association with all EPA programs.

This procedure does not address the collection of light or dense non-aqueous phase liquids (LNAPL or DNAPL) samples, and should be used for aqueous samples only. For sampling NAPLs, the reader is referred to the following EPA publications: DNAPL Site Evaluation (Cohen & Mercer, 1993) and the RCRA Ground-Water Monitoring: Draft Technical Guidance (EPA/530-R-93-001), and references therein.

II. METHOD SUMMARY

The purpose of the low stress purging and sampling procedure is to collect ground water samples from monitoring wells that are representative of ground water conditions in the geological formation. This is accomplished by setting the intake velocity of the sampling pump to a flow rate that limits drawdown inside the well casing.

Sampling at the prescribed (low) flow rate has three primary benefits. First, it minimizes disturbance of sediment in the bottom of the well, thereby producing a sample with low turbidity (i.e., low concentration of suspended particles). Typically, this saves time and analytical costs by eliminating the need for collecting and analyzing an additional filtered sample from the same well. Second, this procedure

minimizes aeration of the ground water during sample collection, which improves the sample quality for VOC analysis. Third, in most cases the procedure significantly reduces the volume of ground water purged from a well and the costs associated with its proper treatment and disposal.

III. ADDRESSING POTENTIAL PROBLEMS

Problems that may be encountered using this technique include a) difficulty in sampling wells with insufficient yield; b) failure of one or more key indicator parameters to stabilize; c) cascading of water and/or formation of air bubbles in the tubing; and d) cross-contamination between wells.

Insufficient Yield

Wells with insufficient yield (i.e., low recharge rate of the well) may dewater during purging. Care should be taken to avoid loss of pressure in the tubing line due to dewatering of the well below the level of the pump's intake. Purging should be interrupted before the water level in the well drops below the top of the pump, as this may induce cascading of the sand pack. Pumping the well dry should therefore be avoided to the extent possible in all cases. Sampling should commence as soon as the volume in the well has recovered sufficiently to allow collection of samples. Alternatively, ground water samples may be obtained with techniques designed for the unsaturated zone, such as lysimeters.

Failure to Stabilize Key Indicator Parameters

If one or more key indicator parameters fails to stabilize after 4 hours, one of four options should be considered: a) continue purging in an attempt to achieve stabilization; b) discontinue purging, do not collect samples, and document attempts to reach stabilization in the log book; c) discontinue purging, collect samples, and document attempts to reach stabilization in the log book; or d) Secure the well, purge and collect samples the next day (preferred). The key indicator parameter for samples to be analyzed for VOCs is dissolved oxygen. The key indicator parameter for all other samples is turbidity.

Cascading

To prevent cascading and/or air bubble formation in the tubing, care should be taken to ensure that the flow rate is sufficient to maintain pump suction. Minimize the length and diameter of tubing (i.e., 1/4

or 3/8 inch ID) to ensure that the tubing remains filled with ground water during sampling.

Cross-Contamination

To prevent cross-contamination between wells, it is strongly recommended that dedicated, in-place pumps be used. As an alternative, the potential for cross-contamination can be reduced by performing the more thorough "daily" decontamination procedures between sampling of each well in addition to the start of each sampling day (see Section VII, below).

Equipment Failure

Adequate equipment should be on-hand so that equipment failures do not adversely impact sampling activities.

IV. PLANNING DOCUMENTATION AND EQUIPMENT

- Approved site-specific Field Sampling Plan/Quality Assurance Project Plan (QAPP). This plan must specify the type of pump and other equipment to be used. The QAPP must also specify the depth to which the pump intake should be lowered in each well. Generally, the target depth will correspond to the mid-point of the most permeable zone in the screened interval. Borehole geologic and geophysical logs can be used to help select the most permeable zone. However, in some cases, other criteria may be used to select the target depth for the pump intake. In all cases, the target depth must be approved by the EPA hydrogeologist or EPA project scientist.

- Well construction data, location map, field data from last sampling event.

- Polyethylene sheeting.

- Flame Ionization Detector (FID) and Photo Ionization Detector (PID).

- Adjustable rate, positive displacement ground water sampling pump (e.g., centrifugal or bladder pumps constructed of stainless steel or Teflon). A peristaltic pump may only be used for inorganic sample collection.

- Interface probe or equivalent device for determining the presence or absence of NAPL.

- Teflon or Teflon-lined polyethylene tubing to collect samples for organic analysis. Teflon or Teflon-lined polyethylene, PVC, Tygon or polyethylene tubing to collect samples for inorganic analysis. Sufficient tubing of the appropriate material must be available so that each well has dedicated tubing.

- Water level measuring device, minimum 0.01 foot accuracy, (electronic preferred for tracking water level drawdown during all pumping operations).

- Flow measurement supplies (e.g., graduated cylinder and stop watch or in-line flow meter).
- Power source (generator, nitrogen tank, etc.).
- Monitoring instruments for indicator parameters. Eh and dissolved oxygen must be monitored in-line using an instrument with a continuous readout display. Specific conductance, pH, and temperature may be monitored either in-line or using separate probes. A nephalometer is used to measure turbidity.

- Decontamination supplies (see Section VII, below).

- Logbook (see Section VIII, below).

- Sample bottles.

- Sample preservation supplies (as required by the analytical methods).

- Sample tags or labels, chain of custody.

V. SAMPLING PROCEDURES

Pre-Sampling Activities

1. Start at the well known or believed to have the least contaminated ground water and proceed systematically to the well with the most contaminated ground water. Check the well, the lock, and the locking cap for damage or evidence of tampering. Record observations.

2. Lay out sheet of polyethylene for placement of monitoring and sampling equipment.

3. Measure VOCs at the rim of the unopened well with a PID and FID instrument and record the reading in the field log book.

4. Remove well cap.

5. Measure VOCs at the rim of the opened well with a PID and an FID instrument and record the reading in the field log book.
6. If the well casing does not have a reference point (usually a V-cut or indelible mark in the well casing), make one. Note that the reference point should be surveyed for correction of ground water elevations to the mean geodesic datum (MSL).

7. Measure and record the depth to water (to 0.01 ft) in all wells to be sampled prior to purging. Care should be taken to minimize disturbance in the water column and dislodging of any particulate matter attached to the sides or settled at the bottom of the well.

8. If desired, measure and record the depth of any NAPLs using an interface probe. Care should be taken to minimize disturbance of any sediment that has accumulated at the bottom of the well. Record the observations in the log book. If LNAPLs and/or DNAPLs are detected, install the pump at this time, as described in step 9, below. Allow the well to sit for several days between the measurement or sampling of any DNAPLs and the low-stress purging and sampling of the ground water.

Sampling Procedures

9. Install Pump: Slowly lower the pump, safety cable, tubing and electrical lines into the well to the depth specified for that well in the EPA-approved QAPP or a depth otherwise approved by the EPA hydrogeologist or EPA project scientist. The pump intake must be kept at least two (2) feet above the bottom of the well to prevent disturbance and resuspension of any sediment or NAPL present in the bottom of the well. Record the depth to which the pump is lowered.

10. Measure Water Level: Before starting the pump, measure the water level again with the pump in the well. Leave the water level measuring device in the well.

11. Purge Well: Start pumping the well at 200 to 500 milliliters per minute (ml/min). The water level should be monitored approximately every five minutes. Ideally, a steady flow rate should be maintained that results in a stabilized water level (drawdown of 0.3 ft or less). Pumping rates should, if needed, be reduced to the minimum capabilities of the pump to ensure stabilization of the water level. As noted above,

care should be taken to maintain pump suction and to avoid entrainment of air in the tubing. Record each adjustment made to the pumping rate and the water level measured immediately after each adjustment.

12. Monitor Indicator Parameters: During purging of the well, monitor and record the field indicator parameters (turbidity, temperature, specific conductance, pH, Eh, and DO) approximately every five minutes. The well is considered stabilized and ready for sample collection when the indicator parameters have stabilized for three consecutive readings as follows (Puls and Barcelona, 1996):

    ±0.1 for pH
    ±3% for specific conductance (conductivity)
    ±10 mv for redox potential
    ±10% for DO and turbidity

    Dissolved oxygen and turbidity usually require the longest time to achieve stabilization. The pump must not be removed from the well between purging and sampling.

13. Collect Samples: Collect samples at a flow rate between 100 and 250 ml/min and such that drawdown of the water level within the well does not exceed the maximum allowable drawdown of 0.3 ft. VOC samples must be collected first and directly into sample containers. All sample containers should be filled with minimal turbulence by allowing the ground water to flow from the tubing gently down the inside of the container.

    Ground water samples to be analyzed for volatile organic compounds (VOCs) require pH adjustment. The appropriate EPA Program Guidance should be consulted to determine whether pH adjustment is necessary. If pH adjustment is necessary for VOC sample preservation, the amount of acid to be added to each sample vial prior to sampling should be determined, drop by drop, on a separate and equal volume of water (e.g., 40 ml). Ground water purged from the well prior to sampling can be used for this purpose.

14. Remove Pump and Tubing: After collection of the samples, the tubing, unless permanently installed, must be properly discarded or dedicated to the well for resampling by hanging the tubing inside the well.

15. Measure and record well depth.

16. Close and lock the well.

VI. FIELD QUALITY CONTROL SAMPLES

Quality control samples must be collected to determine if sample collection and handling procedures have adversely affected the quality of the ground water samples. The appropriate EPA Program Guidance should be consulted in preparing the field QC sample requirements of the site-specific QAPP.

All field quality control samples must be prepared exactly as regular investigation samples with regard to sample volume, containers, and preservation. The following quality control samples should be collected during the sampling event:

- Field duplicates
- Trip blanks for VOCs only
- Equipment blank (not necessary if equipment is dedicated to the well)

As noted above, ground water samples should be collected systematically from wells with the lowest level of contamination through to wells with highest level of contamination. The equipment blank should be collected after sampling from the most contaminated well.

VII. DECONTAMINATION

Non-disposable sampling equipment, including the pump and support cable and electrical wires which contact the sample, must be decontaminated thoroughly each day before use (“daily decon”) and after each well is sampled (“between-well decon”). Dedicated, in-place pumps and tubing must be thoroughly decontaminated using “daily decon” procedures (see #17, below) prior to their initial use. For centrifugal pumps, it is strongly recommended that non-disposable sampling equipment, including the pump and support cable and electrical wires in contact with the sample, be decontaminated thoroughly each day before use (“daily decon”).

EPA’s field experience indicates that the life of centrifugal pumps may be extended by removing entrained grit. This also permits inspection and replacement of the cooling water in centrifugal pumps. All non-dedicated sampling equipment (pumps, tubing, etc.) must be decontaminated after each well is sampled (“between-well decon,” see #18 below).

17. **Daily Decon**

A) Pre-rinse: Operate pump in a deep basin containing 8 to 10 gallons of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

B) Wash: Operate pump in a deep basin containing 8 to 10 gallons of a non-phosphate detergent solution, such as Alconox, for 5 minutes and flush other equipment with fresh detergent solution for 5 minutes. Use the detergent sparingly.

C) Rinse: Operate pump in a deep basin of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

D) Disassemble pump.

E) Wash pump parts: Place the disassembled parts of the pump into a deep basin containing 8 to 10 gallons of non-phosphate detergent solution. Scrub all pump parts with a test tube brush.

F) Rinse pump parts with potable water.

G) Rinse the following pump parts with distilled/ deionized water: inlet screen, the shaft, the suction interconnector, the motor lead assembly, and the stator housing.

H) Place impeller assembly in a large glass beaker and rinse with 1% nitric acid (HNO_3).

I) Rinse impeller assembly with potable water.

J) Place impeller assembly in a large glass bleaker and rinse with isopropanol.

K) Rinse impeller assembly with distilled/deionized water.

18. **Between-Well Decon**

A) Pre-rinse: Operate pump in a deep basin containing 8 to 10 gallons of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.
B) Wash: Operate pump in a deep basin containing 8 to 10 gallons of a non-phosphate detergent solution, such as Alconox, for 5 minutes and flush other equipment with fresh detergent solution for 5 minutes. Use the detergent sparingly.

C) Rinse: Operate pump in a deep basin of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

D) Final Rinse: Operate pump in a deep basin of distilled/deionized water to pump out 1 to 2 gallons of this final rinse water.

VIII. FIELD LOG BOOK

A field log book must be kept each time ground water monitoring activities are conducted in the field. The field log book should document the following:

- Well identification number and physical condition.
- Well depth, and measurement technique.
- Static water level depth, date, time, and measurement technique.
- Presence and thickness of immiscible liquid layers and detection method.
- Collection method for immiscible liquid layers.
- Pumping rate, drawdown, indicator parameters values, and clock time, at three to five minute intervals; calculate or measure total volume pumped.
- Well sampling sequence and time of sample collection.
- Types of sample bottles used and sample identification numbers.
- Preservatives used.
- Parameters requested for analysis.
- Field observations of sampling event.
- Name of sample collector(s).
- Weather conditions.
- QA/QC data for field instruments.

IX. REFERENCES

Cohen, R.M. and J.W. Mercer, 1993, DNAPL Site Evaluation, C.K. Smoley Press, Boca Raton, Florida.

Puls, R.W. and M.J. Barcelona, 1996, Low-Flow (Minimal Drawdown) Ground-water Sampling Procedures, EPA/540/S-95/504.

U.S. EPA, 1993, RCRA Ground-Water Monitoring: Draft Technical Guidance, EPA/530-R-93-001.

U.S. EPA Region II, 1989, CERCLA Quality Assurance Manual.

Hg MW: 200.59 CAS: 7439-97-6 RTECS: OV4550000

METHOD: 6009, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : C 0.1 mg/m^3 (skin)
NIOSH: 0.05 mg/m^3 (skin)
ACGIH: 0.025 mg/m^3 (skin)

PROPERTIES: liquid; d 13.55 g/mL @ 20 °C; BP 356 °C; HP -39 °C; VP 0.16 Pa (0.0012 mm Hg; 13.2 mg/m^3) @ 20 °C; Vapor Density (air=1) 7.0

SYNONYMS: quicksilver

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Hopcalite in single section, 200 mg)

FLOW RATE: 0.15 to 0.25 L/min

VOL-MIN: 2 L @ 0.5 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 30 days @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: at least 3 per set

ACCURACY

RANGE STUDIED: 0.002 to 0.8 mg/m^3 [2] (10-L samples)

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, COLD VAPOR

ANALYTE: elemental mercury

DESORPTION: conc. HNO_3/HCl @ 25 °C, dilute to 50 mL

WAVELENGTH: 253.7 nm

CALIBRATION: standard solutions of Hg^{2+} in 1% HNO_3

RANGE: 0.1 to 1.2 µg per sample

ESTIMATED LOD: 0.03 µg per sample

PRECISION ($\bar{S}_r$): 0.042 @ 0.9 to 3 µg per sample [4]

APPLICABILITY: The working range us 0.01 to 0.5 mg/m^3 for a 10-L air sample. The sorbent material irreversibly collects elemental mercury. A prefilter can be used to exclude particulate mercury species from the sample. The prefilter can be analyzed by similar methodology. The method has been used in numerous field surveys [3].

INTERFERENCES: Inorganic and organic mercury compounds may cause a positive interference. Oxidizing gases, including chlorine, do not interfere.

OTHER METHODS: This replaces method 6000 and its predecessors, which required a specialized desorption apparatus [4,5,6]. This method is based on the method of Rathje and Marcero [7] and is similar to the OSHA method ID 145H [2].

REAGENTS:

1. Water, organics-free, deionized.
2. Hydrochloric acid (HCl), conc.
3. Nitric acid (HNO_3), conc.
4. Mercuric oxide, reagent grade, dry.
5. Calibration stock solution, Hg^{2+}, 1000 µg/mL. Commercially available or dissolve 1.0798 g of dry mercuric oxide (HgO) in 50 mL of 1:1 hydrochloric acid, then dilute to 1 L with deionized water.
6. Intermediate mercury standard, 1 µg/mL. Place 0.1 mL 1000 µg/mL stock into a 100 mL volumetric containing 10 mL deionized water and 1 mL hydrochloric acid. Dilute to volume with deionized water. Prepare fresh daily.
7. Stannous chloride, reagent grade, 10% in 1:1 HCl. Dissolve 20 g stannous chloride in 100 mL conc. HCl. Slowly add this solution to 100 mL deionized water and mix well. Prepare fresh daily.
8. Nitric acid, 1% (w/v). Dilute 14 mL conc. HNO_3 to 1 L with deionized water.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing one section of 200 mg Hopcalite held in place by glass wool plugs (SKC, Inc., Cat. #226-17-1A, or equivalent).
   NOTE: A 37-mm, cellulose ester membrane filter in a cassette preceding the sorbent may be used if particulate mercury is to be determined separately.
2. Personal sampling pump, 0.15 to 0.25 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with cold vapor generation system (see Appendix) or cold vapor mercury analysis system.*
4. Strip chart recorder, or integrator.
5. Flasks, volumetric, 50-mL, and 100-mL.
6. Pipet, 5-mL, 20-mL, others as needed.
7. Micropipet, 10- to 1000-µL.
8. Bottles, biological oxygen demand (BOD), 300-mL.

* See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Mercury is readily absorbed by inhalation and contact with the skin. Operate the mercury system in a hood, or bubble vented mercury through a mercury scrubber.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known rate of 0.15 to 0.25 L/min for a total sample size between 2 and 100 L.
   NOTE: Include a minimum of three unopened sampling tubes from the same lot as the samples for use as media blanks.
4. Cap sampler and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the Hopcalite sorbent and the front glass wool plug from each sampler in separate 50-mL volumetric flasks.
6. Add 2.5 mL conc. HNO_3 followed by 2.5 mL conc. HCl.
   NOTE: The mercury must be in the oxidized state to avoid loss. For this reason, the nitric acid must be added first.
7. Allow the sample to stand for 1 h or until the black Hopcalite sorbent is dissolved. The solution will turn dark brown and may contain undissolved material.
8. Carefully dilute to 50 mL with deionized water. (Final solution is blue to blue-green).
9. Using a volumetric pipet, transfer 20 mL of the sample to a BOD bottle containing 80 mL of deionized water. If the amount of mercury in the sample is expected to exceed the standards, a smaller aliquot may be taken, and the volume of acid adjusted accordingly. The final volume in

the BOD bottle must be 100 mL. To prevent possible loss of mercury during transfer, place the pipet tip below the surface of the liquid in the BOD bottle.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a minimum of two series (six levels each) of working standards covering the range 0.01 to 0.5 µg Hg per aliquot by adding known amounts of the intermediate standard to BOD bottles containing enough 1% nitric acid to bring the final volume to 100 mL.
11. Analyze the working standards together with the samples and blanks (steps 13 through 16). Analyze full set of standards at the beginning of the run, and a second set at the end of the run. Additional standards may be run intermediately during the analysis to confirm instrument response.
12. Prepare calibration graph (peak height vs. solution concentration, µg/sample).

MEASUREMENT:

13. Zero the spectrophotometer by removing the bubbler from the BOD bottle, allowing the baseline on the recorder to stabilize.
14. Place the bubbler in a BOD bottle containing 0.5 µg mercury in 100 mL 1% nitric acid. Adjust the spectrophotometer so that it will give a 75% to full-scale deflection of the recorder.
15. Vent the mercury vapor from the system.
16. Analyze standards, samples and blanks (including media blanks).
    a. Remove the bubbler from the BOD bottle.
    b. Rinse the bubbler with deionized water.
    c. Allow the recorder tracing to establish a stable baseline.
    d. Remove the stopper from the BOD bottle containing the next sample to be analyzed. Gently swirl the BOD bottle.
    e. Quickly add 5 mL 10% stannous chloride solution.
    f. Quickly place the bubbler into the BOD bottle.
    g. Allow the spectrophotometer to attain maximum absorbance.
    h. Vent the mercury vapor from the system.
    i. Place the bubbler into an empty BOD bottle. Continue venting the mercury until a stable baseline is obtained.
    j. Close the mercury vent.

CALCULATIONS:

17. Calculate the amount of mercury in the sample aliquot (W, µg) from the calibration graph.
18. Calculate the concentration C (mg/m ^{3}), of mercury in the air volume sampled, V (L):

$$C = \frac{W \cdot \frac{V_s}{V_a} - B}{V}.$$

Where: Vs = original sample volume (step 8; normally 50 mL)
Va = aliquot volume (step 9; normally 20 mL)
B = average amount of mercury present in the media blanks

EVALUATION OF METHOD:

Rathje and Marcero originally used Hopcalite (MSA, Inc.) as the sorbent material [7]. Later, Hopcalite was shown superior to other methods for the determination of mercury vapor [8]. Atmospheres of mercury vapor for the study were dynamically generated in the range 0.05 to 0.2 mg/m ^{3} and an adsorbent tube loading of 1 to 7 µg was used. The Hydrar material sometimes used is similar to Hopcalite. No significant difference in the laboratory analysis of mercury collected on the two sorbent materials was observed [9]. OSHA also validated a method for mercury using Hydrar [2]. An average 99% recovery, with $\bar{S}r = 0.042$, was seen for 18 samples with known amounts (0.9 to 3 µg) of mercury added (as $Hg(NO_3)_2$) [10]. No change in recovery was seen for samples stored up to 3 weeks at room temperature or up to 3 months at -15 °C; longer storage times were not investigated [10].

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METHOD WRITTEN BY:

Keith R. Nicholson and Michael R. Steele, DataChem Laboratories, Inc., Salt Lake City, Utah, under NIOSH contract No. 200-87-2533.

APPENDIX: COLD VAPOR MERCURY ANALYSIS SYSTEM

1. The valve should direct the vented vapors to a hood or to a mercury scrubber system.
2. When the valve is opened to "Vent" the peristaltic pump should draw room air. Place a Hopcalite tube in the air intake to eliminate any mercury that may be present.
3. Adjust the peristaltic pump to a flow that will create a steady stream of bubbles in the BOD bottle, but not so great that solution droplets enter the tubing to the quartz cell.
4. If water vapor condenses in the quartz cell, heat the cell slightly above room temperature by wrapping it with a heating coil and attaching a variable transformer.
5. The bubbler consists of a glass tube with a bulb at the bottom, slightly above the bottom of the BOD bottle. The bulb contains several perforations to allow air to escape into the solution (in a stream of small bubbles). A second tube is provided to allow the exit of the vapor. The open end of the second tube is well above the surface of the liquid in the bottle. The two tubes are fixed into a stoppering device (preferably ground glass) which fits into the top of the bottle. A coarse glass frit can be used in place of the bulb on the first tube. However, it is more difficult to prevent contamination when a frit is used.
6. Replace the flexible tubing (Tygon or equivalent) used to connect the bubbler, cell, and pump periodically to prevent contamination from adsorbed mercury.

LEAD by Flame AAS 7082

Pb MW: 207.19 (Pb) CAS: 7439-92-1 (Pb) RTECS: OF7525000 (Pb)
223.19 (PbO) 1317-36-8 (PbO) OG1750000 (PbO)

METHOD: 7082, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984 Issue 2: 15 August 1994**

OSHA : 0.05 mg/m^3
NIOSH: <0.1 mg/m^3; blood Pb ≤60 µg/100 g
ACGIH: 0.05 mg/m^3

PROPERTIES: soft metal;
d 11.3 g/cm^3; MP 327.5 °C
valences +2, +4 in salts

SYNONYMS: elemental lead and lead compounds except alkyl lead

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (0.8-µm cellulose ester membrane)	**TECHNIQUE:**	ATOMIC ABSORPTION SPECTROPHOTOMETER, FLAME
FLOW RATE:	1 to 4 L/min	**ANALYTE:**	lead
VOL-MIN:	200 L @ 0.05 mg/m^3	**ASHING:**	conc. HNO_3, 6 mL + 30% H_2O_2, 1 mL; 140 °C
-MAX:	1500 L		
SHIPMENT:	routine	**FINAL SOLUTION:**	10% HNO_3, 10 mL
SAMPLE STABILITY:	stable	**FLAME:**	air-acetylene, oxidizing
BLANKS:	2 to 10 field blanks per set	**WAVELENGTH:**	283.3 nm
ACCURACY		**BACKGROUND CORRECTION:**	D_2 or H_2 lamp, or Zeeman
RANGE STUDIED:	0.13 to 0.4 mg/m^3 [1]; 0.15 to 1.7 mg/m^3 (fume) [2]	**CALIBRATION:**	Pb^{2+} in 10% HNO_3
BIAS:	− 3.1%	**RANGE**	10 to 200 µg per sample [2,3]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.072 [1]; 0.068 (fume) [2]	**ESTIMATED LOD:**	2.6 µg per sample [4]
ACCURACY:	± 17.6%	**PRECISION ($\bar{S}_r$):**	0.03 [1]

APPLICABILITY: The working range is 0.05 to >1 mg/m^3 for a 200-L air sample. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for additional elements.

INTERFERENCES: Use D_2 or H_2 continuum or Zeeman background correction to control flame or molecular absorption. High concentrations of calcium, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be corrected.

OTHER METHODS: This method combines and replaces P&CAM 173 [3] and S341 [4,5] for lead. Method 7300 (ICP-AES) and 7105 (AAS/GF) are alternate analytical methods. Method 7505 is specific for lead sulfide. The following have not been revised: the dithizone method, which appears in P&CAM 102 [5] and the lead criteria document [6]; and P&CAM 191 (ASV) [7].

REAGENTS:

1. Nitric acid, conc.*
2. Nitric acid, 10% (v/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O_2 (w/w), reagent grade.*
4. Calibration stock solution, 1000 µg/mL Pb. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable ≥ one year.
5. Air, compressed, filtered.
6. Acetylene
7. Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Cellulose ester filter, 0.8 µm pore size, 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic Absorption Spectrophotometer with an air-acetylene burner head and background correction.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for air and acetylene.
6. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.**
7. Volumetric flasks, 10- and 100-mL.**
8. Assorted volumetric pipets as needed.**
9. Hotplate, surface temperature 140°C.
10. Bottles, polyethylene, 100-mL.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Concentrated nitric acid is an irritant and may burn skin. Perform all acid digestions in a fume hood. Hydrogen peroxide is a strong oxidizing agent, a strong irritant, and corrosive to the skin. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 h for a total sample size of 200 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE 1: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [4]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

NOTE 2: The Appendix gives a microwave digestion procedure which may be necessary for complete recovery of lead from some matrices, especially epoxy-based paint.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO_3, and 1 mL 30% H_2O_2 and cover with a watchglass. Start reagent blanks at this step.
   NOTE: If PbO_2 is not present in the sample, the 30% H_2O_2 need not be added [2,4].
5. Heat on 140 °C hotplate until volume is reduced to about 0.5 mL.
6. Repeat two more times using 2 mL conc. HNO_3 and 1 mL 30% H_2O_2 each time.
7. Heat on 140 °C hotplate until ca. 0.5 mL liquid remains.
8. When sample is dry, rinse the watchglass and walls of the beaker with 3 to 5 mL 10% HNO_3. Allow the solution to evaporate to dryness.
9. Cool each beaker and dissolve the residues in 1 mL conc. HNO_3.
10. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

NOTE: If the concentration (M) of any of the following is expected to exceed the lead concentration (M) by 10-fold or more, add 1 mL 1 M Na_2EDTA to each flask before dilution to volume: CO_3^{2-}, PO_4^{3-}, I^-, F^-, CH_3COO^-. If Ca^{2+} or SO_4^{2-} are present in 10-fold or greater excess, make all standards and samples 1% (w/w) in La^{3+} [3].

CALIBRATION AND QUALITY CONTROL:

11. Prepare a series of working standards covering the range 0.25 to 20 µg/mL Pb (2.5 to 200 µg Pb per sample).
    a. Add aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 10% HNO_3. Store the working standards in polyethylene bottles and prepare fresh weekly.
    b. Analyze the working standards together with the blanks and samples (steps 14 and 15).
    c. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
12. Aspirate a standard for every 10 samples to check for instrument drift.
13. Check recoveries with at least one spiked media blank per 10 samples. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

14. Set spectrophotometer as specified by the manufacturer and to conditions on page 7082-1.
    NOTE: An alternate wavelength is 217.0 nm [8]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D_2 or H_2 continuum, or Zeeman background correction mandatory at that wavelength.
15. Aspirate standards, samples, and blanks. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute with 10% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

16. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of lead in the sample, C_s, and average media blank, C_b, from the calibration graph.
17. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

NOTE: µg/mL ≡ mg/m

EVALUATION OF METHOD:

Method S341 [9] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/m^3 for a 180-L air sample, using generated atmospheres of lead nitrate [1]. Recovery in the range 18 to 72 µg Pb per sample was 98%, and collection efficiency of 0.8-µm mixed cellulose ester filters (Millipore Type AA) was 100% for the aerosols. Subsequent studies on analytical recovery of 200 µg Pb per sample gave the following results [2,4]:

Species	Digestion Method	Analytical Recovery, %
Pb metal	HNO_3 only	92 ± 4
Pb metal	$HNO_3 + H_2O_2$	103 ± 3
PbO	HNO_3 only	93 ± 4
PbS	HNO_3 only	93 ± 5
PbO_2	HNO_3 only	82 ± 3
PbO_2	$HNO_3 + H_2O_2$	100 ± 1
Pb in paint*	HNO_3 only	95 ± 6
Pb in paint*	$HNO_3 + H_2O_2$	95 ± 6

*Standard Reference Material #1579, U.S. National Institute of Standards and Technology.

Additional collection efficiency studies were also done using Gelman GN-4 filters for the collection of Pb fume, which had geometric mean diameter of 0.1 µm [2]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was > 97 ± 2%. Overall precision, $\hat{S}_{rT}$, was 0.072 for lead nitrate aerosol [1,9] and 0.068 for Pb fume [2,4].

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METHOD REVISED BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS; S341 originally validated under NIOSH Contract CDC-94-74-45; additional studies under NIOSH Contract 210-79-0058.

James B. Perkins, David L. Wheeler, and Keith Nicholson, Ph.D., DataChem Laboratories, Salt Lake City, UT, prepared the microwave digestion procedure in the Appendix.

APPENDIX - MICROWAVE DIGESTION FOR LEAD IN PAINT CHIPS (AND OTHER MATRICES)

This procedure is an alternative to the procedure presented in the Sample Preparation section of this method. It provides a rapid, complete acid digestion prior to analysis by flame atomic absorption (FAA), heated graphite furnace atomic absorption (HGFAA), and inductively coupled plasma spectroscopy (ICP) [10].

Apparatus and Material [11-16]

1. Microwave apparatus requirements
   a. The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.
   b. The microwave unit cavity is corrosion resistant as well as ventilated. All electronics are protected against corrosion for safe operation.
   c. The system requires Teflon PFA digestion vessels (120-mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).
   d. A rotating turntable is employed to ensure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.
   e. A safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained [12].
   f. Polymeric volumetric ware in plastic (Teflon or polyethylene), 50- or 100-mL capacity.
   g. Disposable polypropylene filter funnel.
   h. Analytical balance, 300-g capacity, and minimum ± 0.001 g.

Reagents

1. Nitric acid, concentrated, spectroscopy grade.
2. Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water that meets the ASTM Type 2 standard.

Procedure

1. Calibration of Microwave Equipment
   Calibrate microwave equipment in accordance with manufacturer's instructions. If calibration instructions are not available, see EPA Method 3051 [11].
2. All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) nitric acid for a minimum of fifteen minutes, rinsed with reagent water, and dried in a clean environment.
3. Sample Digestion
   a. Tare the Teflon PFA digestion vessel.
   b. Weigh out 0.1 g paint chip sample to the nearest 0.001 g into the tared Teflon PFA sample vessel. With large paint chip samples, measure out a 2 cm^2 piece, weigh to the nearest 0.001 g, and quantitatively transfer it to the vessel.
   c. Add 5.0 ± 0.1 mL concentrated nitric acid to the sample vessel in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the manufacturer's directions. The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Place the vessels in the microwave carrousel. Connect the overflow vessels to the center well of the unit.
   d. Place the vessels evenly distributed in the turntable of the microwave unit using groups of two, six,

or 12 sample vessels. Any vessels containing 5 mL of nitric acid for reagent blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., three samples plus one blank, the remaining vessels should be filled with 5 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity [14]. Irradiate each group of samples to achieve a temperature of 180 °C in five minutes at a pressure of 50 psi. Continue to irradiate to achieve a temperature of 180 °C at 100 psi after 25 minutes. Continue digestion for five minutes. A sample digestion program for 12 samples is presented in the following table.

PROGRAM VARIABLES FOR PAINT CHIPS SAMPLE DIGESTION WITH NITRIC ACID

Stage	(1)	(2)	(3)
Power	90%	90%	0%
Pressure, psi	50	100	0
Run Time, min	10:00	20:00	05:00
Time @ P, min	05:00	15:00	00:00
Temperature	180°C	180°C	0°C
Fan Speed	100%	100%	100%

Number of Vessels:	12
Liquid Volume per Vessel:	5 mL
Sample Weight:	0.1 g

If the analyst wishes to digest other than two, six, or 12 samples at a time, use different values of power as long as they result in the same time and temperature conditions.

e. At the end of the microwave program, allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit. If a loss of sample is detected (e.g., material in overflow collection vessel, liquid outside liner), determine the reason for the loss (e.g., loss of vessel seal integrity, use of a digestion time longer than 30 minutes, too large a sample, or improper heating conditions). Once the source of the loss has been corrected, prepare a new sample beginning at Section 2. If insufficient material is available for reanalysis, dilute remaining digestate and note that some sample loss may have occurred.

f. Uncap and vent each vessel in a fume hood. Add 20 mL reagent water, then reseal vessels and shake to mix thoroughly. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, allow the sample to settle or filter it:

Settling: Allow the sample to stand until the supernatant is clear (usually, overnight is sufficient). If it does not clear, filter the sample.

Filtering: The filtering apparatus must be thoroughly precleaned and rinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

The digestate is now ready for analysis for elements of interest using the appropriate method.

4. Calculations: Report the concentrations based on the actual weight of the original sample.

Hg MW: 200.59 CAS: 7439-97-6 RTECS: OV4550000

METHOD: 6009, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : C 0.1 mg/m^3 (skin)
NIOSH: 0.05 mg/m^3 (skin)
ACGIH: 0.025 mg/m^3 (skin)

PROPERTIES: liquid; d 13.55 g/mL @ 20 °C; BP 356 °C; HP -39 °C; VP 0.16 Pa (0.0012 mm Hg; 13.2 mg/m^3) @ 20 °C; Vapor Density (air=1) 7.0

SYNONYMS: quicksilver

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Hopcalite in single section, 200 mg)

FLOW RATE: 0.15 to 0.25 L/min

VOL-MIN: 2 L @ 0.5 mg/m^3
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: 30 days @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: at least 3 per set

ACCURACY

RANGE STUDIED: 0.002 to 0.8 mg/m^3 [2] (10-L samples)

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION, COLD VAPOR

ANALYTE: elemental mercury

DESORPTION: conc. HNO_3/HCl @ 25 °C, dilute to 50 mL

WAVELENGTH: 253.7 nm

CALIBRATION: standard solutions of Hg^{2+} in 1% HNO_3

RANGE: 0.1 to 1.2 µg per sample

ESTIMATED LOD: 0.03 µg per sample

PRECISION ($\bar{S}_r$): 0.042 @ 0.9 to 3 µg per sample [4]

APPLICABILITY: The working range us 0.01 to 0.5 mg/m^3 for a 10-L air sample. The sorbent material irreversibly collects elemental mercury. A prefilter can be used to exclude particulate mercury species from the sample. The prefilter can be analyzed by similar methodology. The method has been used in numerous field surveys [3].

INTERFERENCES: Inorganic and organic mercury compounds may cause a positive interference. Oxidizing gases, including chlorine, do not interfere.

OTHER METHODS: This replaces method 6000 and its predecessors, which required a specialized desorption apparatus [4,5,6]. This method is based on the method of Rathje and Marcero [7] and is similar to the OSHA method ID 145H [2].

REAGENTS:

1. Water, organics-free, deionized.
2. Hydrochloric acid (HCl), conc.
3. Nitric acid (HNO_3), conc.
4. Mercuric oxide, reagent grade, dry.
5. Calibration stock solution, Hg^{2+}, 1000 µg/mL. Commercially available or dissolve 1.0798 g of dry mercuric oxide (HgO) in 50 mL of 1:1 hydrochloric acid, then dilute to 1 L with deionized water.
6. Intermediate mercury standard, 1 µg/mL. Place 0.1 mL 1000 µg/mL stock into a 100 mL volumetric containing 10 mL deionized water and 1 mL hydrochloric acid. Dilute to volume with deionized water. Prepare fresh daily.
7. Stannous chloride, reagent grade, 10% in 1:1 HCl. Dissolve 20 g stannous chloride in 100 mL conc. HCl. Slowly add this solution to 100 mL deionized water and mix well. Prepare fresh daily.
8. Nitric acid, 1% (w/v). Dilute 14 mL conc. HNO_3 to 1 L with deionized water.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame sealed ends with plastic caps, containing one section of 200 mg Hopcalite held in place by glass wool plugs (SKC, Inc., Cat. #226-17-1A, or equivalent).
   NOTE: A 37-mm, cellulose ester membrane filter in a cassette preceding the sorbent may be used if particulate mercury is to be determined separately.
2. Personal sampling pump, 0.15 to 0.25 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with cold vapor generation system (see Appendix) or cold vapor mercury analysis system.*
4. Strip chart recorder, or integrator.
5. Flasks, volumetric, 50-mL, and 100-mL.
6. Pipet, 5-mL, 20-mL, others as needed.
7. Micropipet, 10- to 1000-µL.
8. Bottles, biological oxygen demand (BOD), 300-mL.

* See SPECIAL PRECAUTIONS

SPECIAL PRECAUTIONS: Mercury is readily absorbed by inhalation and contact with the skin. Operate the mercury system in a hood, or bubble vented mercury through a mercury scrubber.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately prior to sampling. Attach sampler to pump with flexible tubing.
3. Sample at an accurately known rate of 0.15 to 0.25 L/min for a total sample size between 2 and 100 L.
   NOTE: Include a minimum of three unopened sampling tubes from the same lot as the samples for use as media blanks.
4. Cap sampler and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the Hopcalite sorbent and the front glass wool plug from each sampler in separate 50-mL volumetric flasks.
6. Add 2.5 mL conc. HNO_3 followed by 2.5 mL conc. HCl.
   NOTE: The mercury must be in the oxidized state to avoid loss. For this reason, the nitric acid must be added first.
7. Allow the sample to stand for 1 h or until the black Hopcalite sorbent is dissolved. The solution will turn dark brown and may contain undissolved material.
8. Carefully dilute to 50 mL with deionized water. (Final solution is blue to blue-green).
9. Using a volumetric pipet, transfer 20 mL of the sample to a BOD bottle containing 80 mL of deionized water. If the amount of mercury in the sample is expected to exceed the standards, a smaller aliquot may be taken, and the volume of acid adjusted accordingly. The final volume in

the BOD bottle must be 100 mL. To prevent possible loss of mercury during transfer, place the pipet tip below the surface of the liquid in the BOD bottle.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a minimum of two series (six levels each) of working standards covering the range 0.01 to 0.5 µg Hg per aliquot by adding known amounts of the intermediate standard to BOD bottles containing enough 1% nitric acid to bring the final volume to 100 mL.
11. Analyze the working standards together with the samples and blanks (steps 13 through 16). Analyze full set of standards at the beginning of the run, and a second set at the end of the run. Additional standards may be run intermediately during the analysis to confirm instrument response.
12. Prepare calibration graph (peak height vs. solution concentration, µg/sample).

MEASUREMENT:

13. Zero the spectrophotometer by removing the bubbler from the BOD bottle, allowing the baseline on the recorder to stabilize.
14. Place the bubbler in a BOD bottle containing 0.5 µg mercury in 100 mL 1% nitric acid. Adjust the spectrophotometer so that it will give a 75% to full-scale deflection of the recorder.
15. Vent the mercury vapor from the system.
16. Analyze standards, samples and blanks (including media blanks).
    a. Remove the bubbler from the BOD bottle.
    b. Rinse the bubbler with deionized water.
    c. Allow the recorder tracing to establish a stable baseline.
    d. Remove the stopper from the BOD bottle containing the next sample to be analyzed. Gently swirl the BOD bottle.
    e. Quickly add 5 mL 10% stannous chloride solution.
    f. Quickly place the bubbler into the BOD bottle.
    g. Allow the spectrophotometer to attain maximum absorbance.
    h. Vent the mercury vapor from the system.
    i. Place the bubbler into an empty BOD bottle. Continue venting the mercury until a stable baseline is obtained.
    j. Close the mercury vent.

CALCULATIONS:

17. Calculate the amount of mercury in the sample aliquot (W, µg) from the calibration graph.
18. Calculate the concentration C (mg/m ^{3}), of mercury in the air volume sampled, V (L):

$$C = \frac{W \cdot \frac{V_s}{V_a} - B}{V}.$$

Where: Vs = original sample volume (step 8; normally 50 mL)
Va = aliquot volume (step 9; normally 20 mL)
B = average amount of mercury present in the media blanks

EVALUATION OF METHOD:

Rathje and Marcero originally used Hopcalite (MSA, Inc.) as the sorbent material [7]. Later, Hopcalite was shown superior to other methods for the determination of mercury vapor [8]. Atmospheres of mercury vapor for the study were dynamically generated in the range 0.05 to 0.2 mg/m ^{3} and an adsorbent tube loading of 1 to 7 µg was used. The Hydrar material sometimes used is similar to Hopcalite. No significant difference in the laboratory analysis of mercury collected on the two sorbent materials was observed [9]. OSHA also validated a method for mercury using Hydrar [2]. An average 99% recovery, with $\bar{S}r = 0.042$, was seen for 18 samples with known amounts (0.9 to 3 µg) of mercury added (as $Hg(NO_3)_2$) [10]. No change in recovery was seen for samples stored up to 3 weeks at room temperature or up to 3 months at -15 °C; longer storage times were not investigated [10].

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METHOD WRITTEN BY:

Keith R. Nicholson and Michael R. Steele, DataChem Laboratories, Inc., Salt Lake City, Utah, under NIOSH contract No. 200-87-2533.

APPENDIX: COLD VAPOR MERCURY ANALYSIS SYSTEM

1. The valve should direct the vented vapors to a hood or to a mercury scrubber system.
2. When the valve is opened to "Vent" the peristaltic pump should draw room air. Place a Hopcalite tube in the air intake to eliminate any mercury that may be present.
3. Adjust the peristaltic pump to a flow that will create a steady stream of bubbles in the BOD bottle, but not so great that solution droplets enter the tubing to the quartz cell.
4. If water vapor condenses in the quartz cell, heat the cell slightly above room temperature by wrapping it with a heating coil and attaching a variable transformer.
5. The bubbler consists of a glass tube with a bulb at the bottom, slightly above the bottom of the BOD bottle. The bulb contains several perforations to allow air to escape into the solution (in a stream of small bubbles). A second tube is provided to allow the exit of the vapor. The open end of the second tube is well above the surface of the liquid in the bottle. The two tubes are fixed into a stoppering device (preferably ground glass) which fits into the top of the bottle. A coarse glass frit can be used in place of the bulb on the first tube. However, it is more difficult to prevent contamination when a frit is used.
6. Replace the flexible tubing (Tygon or equivalent) used to connect the bubbler, cell, and pump periodically to prevent contamination from adsorbed mercury.

LEAD by Flame AAS 7082

Pb MW: 207.19 (Pb) CAS: 7439-92-1 (Pb) RTECS: OF7525000 (Pb)
223.19 (PbO) 1317-36-8 (PbO) OG1750000 (PbO)

METHOD: 7082, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984 Issue 2: 15 August 1994**

OSHA : 0.05 mg/m^3
NIOSH: <0.1 mg/m^3; blood Pb ≤60 µg/100 g
ACGIH: 0.05 mg/m^3

PROPERTIES: soft metal;
d 11.3 g/cm^3; MP 327.5 °C
valences +2, +4 in salts

SYNONYMS: elemental lead and lead compounds except alkyl lead

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (0.8-µm cellulose ester membrane)	**TECHNIQUE:**	ATOMIC ABSORPTION SPECTROPHOTOMETER, FLAME
FLOW RATE:	1 to 4 L/min	**ANALYTE:**	lead
VOL-MIN:	200 L @ 0.05 mg/m^3	**ASHING:**	conc. HNO_3, 6 mL + 30% H_2O_2, 1 mL; 140 °C
-MAX:	1500 L		
SHIPMENT:	routine	**FINAL SOLUTION:**	10% HNO_3, 10 mL
SAMPLE STABILITY:	stable	**FLAME:**	air-acetylene, oxidizing
BLANKS:	2 to 10 field blanks per set	**WAVELENGTH:**	283.3 nm
ACCURACY		**BACKGROUND CORRECTION:**	D_2 or H_2 lamp, or Zeeman
RANGE STUDIED:	0.13 to 0.4 mg/m^3 [1]; 0.15 to 1.7 mg/m^3 (fume) [2]	**CALIBRATION:**	Pb^{2+} in 10% HNO_3
BIAS:	− 3.1%	**RANGE**	10 to 200 µg per sample [2,3]
OVERALL PRECISION ($\hat{S}_{rT}$):	0.072 [1]; 0.068 (fume) [2]	**ESTIMATED LOD:**	2.6 µg per sample [4]
ACCURACY:	± 17.6%	**PRECISION ($\bar{S}_r$):**	0.03 [1]

APPLICABILITY: The working range is 0.05 to >1 mg/m^3 for a 200-L air sample. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for additional elements.

INTERFERENCES: Use D_2 or H_2 continuum or Zeeman background correction to control flame or molecular absorption. High concentrations of calcium, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be corrected.

OTHER METHODS: This method combines and replaces P&CAM 173 [3] and S341 [4,5] for lead. Method 7300 (ICP-AES) and 7105 (AAS/GF) are alternate analytical methods. Method 7505 is specific for lead sulfide. The following have not been revised: the dithizone method, which appears in P&CAM 102 [5] and the lead criteria document [6]; and P&CAM 191 (ASV) [7].

REAGENTS:

1. Nitric acid, conc.*
2. Nitric acid, 10% (v/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O_2 (w/w), reagent grade.*
4. Calibration stock solution, 1000 µg/mL Pb. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of (1+1) HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable ≥ one year.
5. Air, compressed, filtered.
6. Acetylene
7. Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Cellulose ester filter, 0.8 µm pore size, 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic Absorption Spectrophotometer with an air-acetylene burner head and background correction.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for air and acetylene.
6. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.**
7. Volumetric flasks, 10- and 100-mL.**
8. Assorted volumetric pipets as needed.**
9. Hotplate, surface temperature 140°C.
10. Bottles, polyethylene, 100-mL.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Concentrated nitric acid is an irritant and may burn skin. Perform all acid digestions in a fume hood. Hydrogen peroxide is a strong oxidizing agent, a strong irritant, and corrosive to the skin. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 h for a total sample size of 200 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE 1: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [4]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

NOTE 2: The Appendix gives a microwave digestion procedure which may be necessary for complete recovery of lead from some matrices, especially epoxy-based paint.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO_3, and 1 mL 30% H_2O_2 and cover with a watchglass. Start reagent blanks at this step.
   NOTE: If PbO_2 is not present in the sample, the 30% H_2O_2 need not be added [2,4].
5. Heat on 140 °C hotplate until volume is reduced to about 0.5 mL.
6. Repeat two more times using 2 mL conc. HNO_3 and 1 mL 30% H_2O_2 each time.
7. Heat on 140 °C hotplate until ca. 0.5 mL liquid remains.
8. When sample is dry, rinse the watchglass and walls of the beaker with 3 to 5 mL 10% HNO_3. Allow the solution to evaporate to dryness.
9. Cool each beaker and dissolve the residues in 1 mL conc. HNO_3.
10. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

NOTE: If the concentration (M) of any of the following is expected to exceed the lead concentration (M) by 10-fold or more, add 1 mL 1 M Na_2EDTA to each flask before dilution to volume: CO_3^{2-}, PO_4^{3-}, I^-, F^-, CH_3COO^-. If Ca^{2+} or SO_4^{2-} are present in 10-fold or greater excess, make all standards and samples 1% (w/w) in La^{3+} [3].

CALIBRATION AND QUALITY CONTROL:

11. Prepare a series of working standards covering the range 0.25 to 20 µg/mL Pb (2.5 to 200 µg Pb per sample).
    a. Add aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 10% HNO_3. Store the working standards in polyethylene bottles and prepare fresh weekly.
    b. Analyze the working standards together with the blanks and samples (steps 14 and 15).
    c. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
12. Aspirate a standard for every 10 samples to check for instrument drift.
13. Check recoveries with at least one spiked media blank per 10 samples. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

14. Set spectrophotometer as specified by the manufacturer and to conditions on page 7082-1.
    NOTE: An alternate wavelength is 217.0 nm [8]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D_2 or H_2 continuum, or Zeeman background correction mandatory at that wavelength.
15. Aspirate standards, samples, and blanks. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute with 10% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

16. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of lead in the sample, C_s, and average media blank, C_b, from the calibration graph.
17. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.$$

NOTE: µg/mL ≡ mg/m

EVALUATION OF METHOD:

Method S341 [9] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/m^3 for a 180-L air sample, using generated atmospheres of lead nitrate [1]. Recovery in the range 18 to 72 µg Pb per sample was 98%, and collection efficiency of 0.8-µm mixed cellulose ester filters (Millipore Type AA) was 100% for the aerosols. Subsequent studies on analytical recovery of 200 µg Pb per sample gave the following results [2,4]:

Species	Digestion Method	Analytical Recovery, %
Pb metal	HNO_3 only	92 ± 4
Pb metal	$HNO_3 + H_2O_2$	103 ± 3
PbO	HNO_3 only	93 ± 4
PbS	HNO_3 only	93 ± 5
PbO_2	HNO_3 only	82 ± 3
PbO_2	$HNO_3 + H_2O_2$	100 ± 1
Pb in paint*	HNO_3 only	95 ± 6
Pb in paint*	$HNO_3 + H_2O_2$	95 ± 6

*Standard Reference Material #1579, U.S. National Institute of Standards and Technology.

Additional collection efficiency studies were also done using Gelman GN-4 filters for the collection of Pb fume, which had geometric mean diameter of 0.1 µm [2]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was > 97 ± 2%. Overall precision, $\hat{S}_{rT}$, was 0.072 for lead nitrate aerosol [1,9] and 0.068 for Pb fume [2,4].

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METHOD REVISED BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS; S341 originally validated under NIOSH Contract CDC-94-74-45; additional studies under NIOSH Contract 210-79-0058.

James B. Perkins, David L. Wheeler, and Keith Nicholson, Ph.D., DataChem Laboratories, Salt Lake City, UT, prepared the microwave digestion procedure in the Appendix.

APPENDIX - MICROWAVE DIGESTION FOR LEAD IN PAINT CHIPS (AND OTHER MATRICES)

This procedure is an alternative to the procedure presented in the Sample Preparation section of this method. It provides a rapid, complete acid digestion prior to analysis by flame atomic absorption (FAA), heated graphite furnace atomic absorption (HGFAA), and inductively coupled plasma spectroscopy (ICP) [10].

Apparatus and Material [11-16]

1. Microwave apparatus requirements
   a. The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.
   b. The microwave unit cavity is corrosion resistant as well as ventilated. All electronics are protected against corrosion for safe operation.
   c. The system requires Teflon PFA digestion vessels (120-mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).
   d. A rotating turntable is employed to ensure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.
   e. A safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained [12].
   f. Polymeric volumetric ware in plastic (Teflon or polyethylene), 50- or 100-mL capacity.
   g. Disposable polypropylene filter funnel.
   h. Analytical balance, 300-g capacity, and minimum ± 0.001 g.

Reagents

1. Nitric acid, concentrated, spectroscopy grade.
2. Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water that meets the ASTM Type 2 standard.

Procedure

1. Calibration of Microwave Equipment
   Calibrate microwave equipment in accordance with manufacturer's instructions. If calibration instructions are not available, see EPA Method 3051 [11].
2. All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) nitric acid for a minimum of fifteen minutes, rinsed with reagent water, and dried in a clean environment.
3. Sample Digestion
   a. Tare the Teflon PFA digestion vessel.
   b. Weigh out 0.1 g paint chip sample to the nearest 0.001 g into the tared Teflon PFA sample vessel. With large paint chip samples, measure out a 2 cm^2 piece, weigh to the nearest 0.001 g, and quantitatively transfer it to the vessel.
   c. Add 5.0 ± 0.1 mL concentrated nitric acid to the sample vessel in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the manufacturer's directions. The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Place the vessels in the microwave carrousel. Connect the overflow vessels to the center well of the unit.
   d. Place the vessels evenly distributed in the turntable of the microwave unit using groups of two, six,

or 12 sample vessels. Any vessels containing 5 mL of nitric acid for reagent blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., three samples plus one blank, the remaining vessels should be filled with 5 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity [14]. Irradiate each group of samples to achieve a temperature of 180 °C in five minutes at a pressure of 50 psi. Continue to irradiate to achieve a temperature of 180 °C at 100 psi after 25 minutes. Continue digestion for five minutes. A sample digestion program for 12 samples is presented in the following table.

PROGRAM VARIABLES FOR PAINT CHIPS SAMPLE DIGESTION WITH NITRIC ACID

Stage	(1)	(2)	(3)
Power	90%	90%	0%
Pressure, psi	50	100	0
Run Time, min	10:00	20:00	05:00
Time @ P, min	05:00	15:00	00:00
Temperature	180°C	180°C	0°C
Fan Speed	100%	100%	100%

Number of Vessels:	12
Liquid Volume per Vessel:	5 mL
Sample Weight:	0.1 g

If the analyst wishes to digest other than two, six, or 12 samples at a time, use different values of power as long as they result in the same time and temperature conditions.

e. At the end of the microwave program, allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit. If a loss of sample is detected (e.g., material in overflow collection vessel, liquid outside liner), determine the reason for the loss (e.g., loss of vessel seal integrity, use of a digestion time longer than 30 minutes, too large a sample, or improper heating conditions). Once the source of the loss has been corrected, prepare a new sample beginning at Section 2. If insufficient material is available for reanalysis, dilute remaining digestate and note that some sample loss may have occurred.

f. Uncap and vent each vessel in a fume hood. Add 20 mL reagent water, then reseal vessels and shake to mix thoroughly. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, allow the sample to settle or filter it:

Settling: Allow the sample to stand until the supernatant is clear (usually, overnight is sufficient). If it does not clear, filter the sample.

Filtering: The filtering apparatus must be thoroughly precleaned and rinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

The digestate is now ready for analysis for elements of interest using the appropriate method.

4. Calculations: Report the concentrations based on the actual weight of the original sample.

REGION I, EPA-NEW ENGLAND

DRAFT
STANDARD OPERATING PROCEDURE
FOR SAMPLING CONCRETE IN THE FIELD

U.S. EPA-NEW ENGLAND
Region I
Quality Assurance Unit Staff
Office of Environmental Measurement and Evaluation

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Region I, EPA New England

Standard Operating Procedure for Sampling Concrete in the Field

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Region I, EPA New England

Standard Operating Procedure for Sampling Concrete in the Field

1.0 Scope and Application

The following Standard Operating Procedure (SOP) describes a concrete sampling technique which uses an impact hammer drill to generate a uniform, finely ground, powder which is easily homogenized, extracted and analyzed. This procedure is primarily geared at providing enough sample for one or two different analyses at a time. That is, the time required to generate sufficient sample for a full sweet of analyses may be impractical. The concrete powder is suitable for all types of environmental analyses, with the exception of volatile compounds, and may be analyzed in the field or at a fixed laboratory. This procedure is applicable for the collection of samples from concrete floors, walls, and ceilings.

The impact hammer drill is far less labor intensive than previous techniques using coring devices, or hammers and chisels. It allows for easy selection of sample location and sample depth. Not only can the project planner control the depth to sample into the concrete, from surface samples (0 - ½ inch) down to a core of the entire slab, but the technique can also be modified to collect samples at discrete depths within the concrete slab.

Another issue with concrete sampling is the fact that the amount of time spent drilling translates into the weight of sample produced. Thus, to maximize sampling time, it is important to know the minimum amount of sample required for each analysis. To do this, the project planner should take the following steps: 1) Use the Data Quality Objective (DQO) process and familiarity with the site to develop the objectives of the sampling project and the depth(s) of sample to be collected. 2) Review the site history and any previous data collected to determined possible contaminants of concern. 3) Establish the action levels for those possible contaminants and determine the appropriate analytical methods (both field and/or fixed laboratory) to meet the DQOs of the project. 4) Based on the detection limits of these methods, determine the amount of sample required for each analysis and the total sample weight require for each sample location (including quality control samples).

As with any environmental data collection project, all aspects of a concrete sampling episode should be well thought out, prior to going out in the field, and thoroughly described in a Quality Assurance Project Plan (QAPP). The QAPP should clearly state the DQOs of the project and document a complete Quality Assurance/Quality Control program to reconcile the data generated with the established DQOs. For more information on these subjects, refer to EPA documents QA/R-5, EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations, and QA/G-4, Guidance for the Data Quality Objective Process.

2.0 Method Summary

A one-inch diameter carbide drill bit is used in a rotary impact hammer drill to generate a fine concrete powder suitable for analysis. The powder is placed in a sample container and homogenized for field or fixed laboratory analysis. The procedure can be used to sample a single depth into the concrete, or may be modified to sample the concrete at distinctly different depth zones. The modified depth sampling procedure is designed to minimize any cross contamination between the sampling zones. If different sampling depths are required, two different diameter drill bits and a vacuum sampling apparatus are employed.

3.0 Health and Safety

Eye and hearing protection are required at all times during sample drilling. A small amount of dust is generated during the drilling process. Proper respiratory protection and/or a dust control system must be in place at all times during sampling.

4.0 Interferences and Potential Problems

Since this sampling technique produces a finely ground uniform powder, physical matrix effects from variations in the sample consistency (i.e., particle size, uniformity, homogeneity, and surface condition) are minimized. Matrix spike analysis of a sample is highly recommended to monitor for any matrix related interferences.

As stated in Section 1.0 above, this sampling procedure is not recommended for volatile organic compound (VOC) analysis. The combination of heat generated during drilling and the exposure of a large amount of surface area will greatly reduce VOC recovery. If low boiling point semi-volatile compounds (i.e., naphthalene) are being analyzed, then the drill speed should be reduced to minimize heat build-up.

5.0 Equipment and Supplies

5.1 Single Depth Concrete Sampling

5.1.1 Rotary impact hammer drill
5.1.2 1-inch diameter carbide drill bits
5.1.3 Stainless steel scoopulas
5.1.4 Stainless steel spoonulas (for collecting sample in deeper holes, >2-inches)
5.1.5 Rectangular aluminum pans (to catch concrete during wall and ceiling sampling)
5.1.6 Gasoline powered generator (if alternative power source is required)

5.2 Multiple Depth Sampling (in addition to all the above)

5.2.1 ½ inch diameter carbide drill bits
5.2.2 Vacuum/sample trap assembly (see Section 7.2 and Figure 1)

5.2.2.1 Vacuum pump
5.2.2.2 2-hole rubber stopper
5.2.2.3 Glass tubing (to fit stopper)
5.2.2.4 Large glass test tubes, or Erlenmeyer flasks, for sample trap (several are suggested)
5.2.2.5 Polyethylene tubing for trap inlet (Tygon tubing may be used for the trap outlet)
5.2.2.6 Pasture pipets
5.2.2.7 Pipe cleaners
5.2.2.8 In-line dust filter (glass fiber filter, or equivalent)

6.0 Sample Containers, Preservation, and Storage

Concrete samples must be collected in glass containers for organic analyses, and may be collected in either glass or plastic containers for inorganic analyses. In general, a 2-ounce sample container with

Teflon-lined cap (wide-mouth jars are preferred) will hold sufficient volume for most analyses. A 2-ounce jar can hold roughly 90 grams sample. Note, samples which require duplicate and/or matrix spike/matrix spike duplicate analyses may require a larger sample container, or additional 2-ounce sample containers.

Organic samples are to be shipped on ice and maintained at 4°C (± 2°C) until the time of extraction and analysis. Inorganic samples may be shipped and stored at room temperature. Refer to 40 CFR Part 136 for guidelines on analysis holding times.

To maintain sample integrity, chain-of-custody procedures must be implemented at the time of sampling to 1) document all sample locations and associated field sample identification numbers, 2) document all quality control samples taken, including field duplicates, split samples for confirmatory analyses, and PE samples, and 3) document the transfer of field samples from field sampler to field chemist or fixed laboratory.

7.0 Procedure

7.1 Single Depth Concrete Sampling

Lock a 1-inch diameter carbide drill bit into the impact hammer drill and plug the drill into an appropriate power source. (A gasoline generator will be needed if electricity is not available.) For easy identification, sample locations may be pre-marked using a crayon or a non-contaminating spray paint. (Note, the actual drilling point must not be marked.) Depending on the appearance of the sample location, or the objectives of the sampling project, it may be desired to wipe the concrete surface with a clean dry cloth prior to drilling. All sampling decisions of this nature should be noted in the sampling logbook. Begin drilling in the designated location. Apply steady even pressure and let the drill do the work. Applying too much pressure will generate excessive heat and dull the drill bit prematurely. The drill will provide a finely ground concrete powder that can be easily collected, homogenized and analyzed. Having several decontaminated impact drill bits on hand will help expedite sampling when numerous sample locations are to be drilled.

Sample Collection

A ½-inch deep hole (using a 1-inch diameter drill bit) generates about 10 grams of concrete powder. Based on this and the action levels for the project, determine the sampling depth, and/or the number of sample holes to be composited, to generate sufficient sample volume for all of the required analyses. (Note, with the absorbency of concrete, a ½-inch deep hole can be considered a surface sample.)

A decontaminated stainless steel scoopula can be used to collect the sample. The powder can either be collected directly from the surface of the concrete and/or the concrete powder can be scraped back into the hole and the less rounded back edge of the scoopula can be used to collect the sample. For holes greater than 2-inches in depth, a stainless steel spoonula will make it easier to collect the sample from the bottom of the hole.
To ensure collection of a representative sample when multiple analyses are required, a concrete sample should always be collected and homogenized in a single container and then divided up into the individual containers for the various analyses or split samples. This is particularly important when sample holes are deep, or when several holes are drilled adjacent to each other to form a sample composite.

Wall and Ceiling Sampling

A team of two samplers will be required for wall and ceiling sampling. The second person will be needed to hold a clean catch surface (i.e., an aluminum pan) below the drill to collect the falling powder. For wall samples, a scoopula, or spoonula, can be used to collect remaining concrete powder from within the hole. For ceiling holes, it may be necessary to drill the hole at an angle so the concrete powder can fall freely in the collection plan (and avoid falling on the drill). Another alternative might be to use the chuck-end of the drill bit and punch a hole through the center of the collection pan. The drill bit is then mounted through the pan and into the drill. Thus, the driller can be drilling straight up while the assistant steadies the pan to catch the falling dust. As a precaution, it may be advantageous to tape a piece of plastic around the drill, just below the chuck, to avoid dust contaminating the body of the drill and entering the mechanical vents. (Note, the plastic should deflect dust from the drill, but be loose enough underneath to allow for proper ventillation.)

7.2 Multiple Depth Concrete Sampling

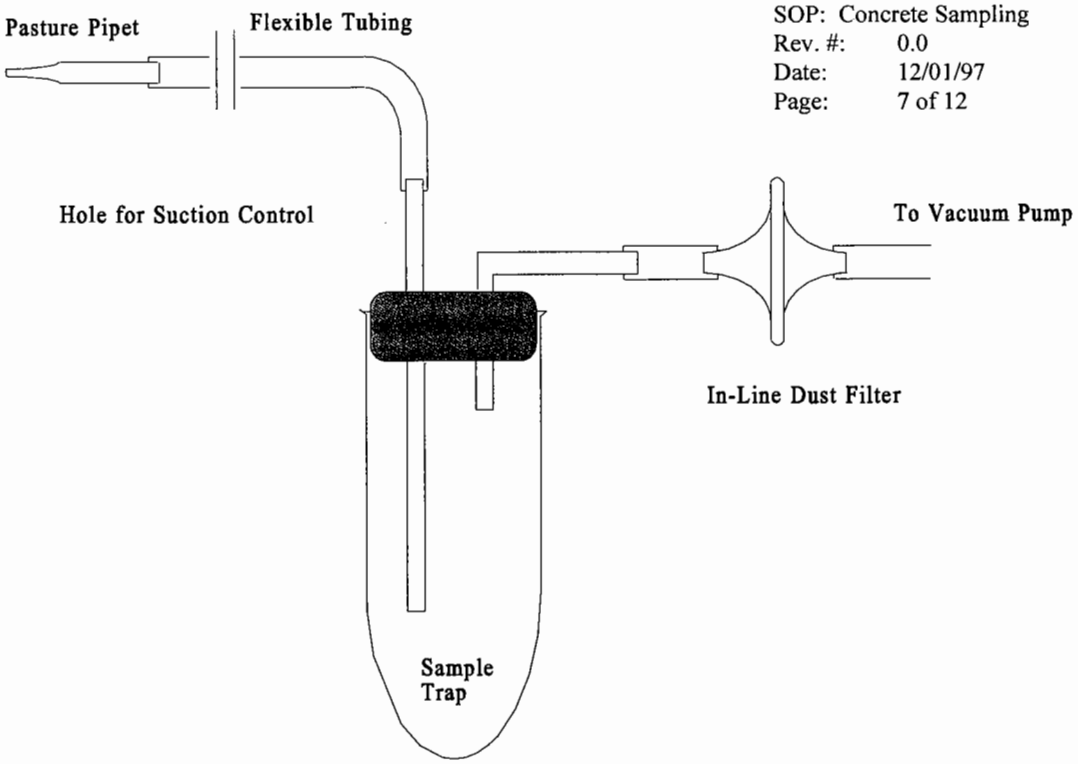
The above method for concrete sampling can also be used to collect samples from different depths within the concrete. To do this, two different sized drill bits (i.e., ½ inch and 1 inch) and a simple vacuum pump with a vacuum trap assembly is required (see Figure 1). First, the 1 inch drill bit is used to drill to the first level and the concrete sample is collected as described in Section 7.1. The vacuum pump is then turned on and the hole is cleaned out using the vacuum trap assembly. The drill bit is then changed to the ½ inch bit and the next depth is drilled out (the ½ inch bit is used to avoid contact with the sides of the first hole). A clean tube or flask is placed on the vacuum trap, and the sample from the second drilling is collected. To go further, the 1 inch drill is used to open up the hole to the second level, the hole is cleared, and then the ½ inch drill is used again to go to a third level, etc. Note, the holes and concrete surface should be vacuumed thoroughly to minimize any cross-contamination between sample depths.

Vacuum Trap Design and Clean-out

The trap presented in Figure 1 is a convenient and thorough way for collecting and removing concrete powder from drilled holes. The trap system is designed to allow for control of the suction from the vacuum pump and easy trap clean-out between samples. Note, by placing a hole in the inlet tube (see Figure 1), a finger on the hand holding the trap can be used to control the suction at the sampling tip. Thus, when this hole is left completely open, there will be no suction, and the sampler can have complete control over where and what to sample. To change-out between samples the following steps should be taken: 1) The pasture pipet and piece of polyethylene tubing at the sample inlet should be replaced with new materials, 2) the portion of the rubber stopper and glass tubing that was in the trap should be wiped down with a clean damp paper towel (wetted with deionized water) and then dried with a fresh paper towel, 3) a clean pipe cleaner should be drawn through the glass inlet tube to remove any concrete dust present, and 4) the glass tube or flask used to collect the sample should swapped out with a clean decontaminated sample trap. Having several clean tubes or flasks on hand will facilitate change-out between samples.

7.3 Decontamination Procedure

Necessary supplies for decontamination include: two small buckets, a scrub brush, potable water, deionized water, a squirt bottle for the deionized water, and paper towels. The first bucket contains a soap and potable water solution, and the second bucket contains just potable water. Place all used drill



bits and utensils in the soap and water bucket. Scrub each piece thoroughly using the scrub brush. Note, the concrete powder does cling to the metal surfaces, so care should be taken during this step, especially with the twists and curves of the drill bits. Next, rinse each piece in the potable water bucket, and follow with a deionized water rinse from the squirt bottle. Place the deionized water rinsed pieces on clean paper towels and individually dry and inspect each piece. Note, all pieces should be dry prior to reuse.

8.0 Field Documentation

All Site related documentation and reports generated from concrete sampling should be maintained in the central Site file. If personal logbooks are used, legible copies of all pertinent pages must be placed in the Site file.

8.1 Field Logbooks

All field documentation should be maintained in bound logbooks with numbered pages. If loose-leaf logsheets are used to document site activities, extra care should be taken in keep track of all logsheets. The original copy of all logsheets should be maintained in the central Site file. Note, all sample locations must be documented by tying in their location to a detailed site map, or by using two or more permanent landmarks. The following information should be documented in the field logbooks:

- Site name and location,
- EPA Site Manager,
- Name and affiliation of field samplers (EPA, Contractor company name, etc.),
- Sampling date,
- Sample locations and IDs,
- Sampling times and depths, and
- Other pertinent information or comments

8.2 Sample Labeling and Chain-of-Custody

8.2.1 Sample Labels

Sample labels will be affixed to all sample containers. Labels must contain the following information:

- Project name,
- Sample number, and/or location
- Date and time of sampling,
- Analysis,
- Preservation, and
- Sampler's name.

8.2.2 Chain-of-Custody

All samples must be traced from collection, to shipment, to laboratory receipt and laboratory custody. The Chain-of-Custody (COC) Record is a multi-part form that is initiated as samples are acquired and accompanies a sample (or group of samples) as they are transferred from person to person. The COC form is signed by all individuals responsible for sampling, sample transport, and laboratory receipt. (Note, overnight deliver services, often used with sample transport, are exempt from having to sign the COC form. However, copies of all shipping invoices must be kept with the COC documentation.) One copy of the COC is retained by the field sampling crew, while the original (top, signed copy) and remaining carbonless copies are placed in a zip-lock bag and taped to the inside lid of the shipping cooler. If multiple coolers are required for a sample shipment to a single laboratory, the COC need only be sent with one of the coolers. The COC should state how many coolers are included with the shipment. All sample shipments to different laboratories require individual COC forms. The original COC form accompanies the samples until the project is complete, and is then kept in the permanent project file. A copy of the COC is also kept with the project manager, the laboratory manager, and attached to the data package.

8.2.3 Custody Seal

The Custody seal is an adhesive-backed label which is also part of the chain-of-custody process. The custody seal is used to prevent tampering with the samples after they have been collected in the field and sealed in coolers for transit to the laboratory. The Custody seals are signed and dated by a sampler and affixed across the opening edges of each cooler containing samples. Clear packing tape should be wrapped around the cooler, and over the Custody seal, to secure the cooler and avoid accidental tampering with the Custody seal.

9.0 Quality Assurance and Quality Control (QA/QC)

A solid QA/QC program is essential to establishing the quality of the data generated so that proper project decisions can be made. The following are key quality control elements which should be incorporated into a concrete sampling and analytical program.

9.1 Equipment Blanks

An equipment blank should be performed on decontaminated drill bits and collection utensils at a frequency of 1 per 20 samples or 1 per day, whichever is greater. To prepare the equipment blank, place the decontaminated drill bit and utensils in a large clean stainless steel bowl. Pour sufficient deionized water into the bowl to fill all of the required sample containers. Next, stir the drill bit and utensils in the bowl with a clean utensil to thoroughly mix the blank. Finally, decant off the equipment blank into the sample containers. Note, a clean funnel may help to pour off the equipment blank into the containers.

9.2 Field Duplicates

Field duplicates are samples collected adjacent to each other (collocated) at the same sample location (not two aliquots of the same sample). Field duplicates not only help provide an indicator of overall precision, but measure the cumulative effects of both the field and analytical precision, and also measure the representativeness of the sample. Field duplicates must be prepared and analyzed at a frequency of 1 per 20 samples or 1 per non-related concrete matrix, whichever is greater. An example of a non-related concrete matrix might be the investigation of two different types of chemical spills.

Calculate the Relative Percent Difference (RPD) between the sample and its duplicate using Equation 1.

$$RPD = \frac{|S - D|}{\frac{(S + D)}{2}} x\,100$$

Equation 1
Where:

S = Original sample result
D = Duplicate sample result

The following general guidelines have been established for field duplicate criteria:

- If both the original and field duplicate values are ≥ practical quantitation limit (PQL), then the control limit for RPD is ≤50%,
- If one or both values are < PQL, then do not assess the RPD.

If more rigorous field duplicate criteria are needed to achieve project DQOs, then that criteria should be documented in the project QAPP.

If the field duplicate criteria specified above are not met, then flag that target element with an "*" on the final report for both the original and field duplicate samples. Report both the original and field duplicate analyses; do not report the average. Field duplicate samples should should be indicated on the sample ID. For example, the sample ID can contain the the suffix "FD".

9.3 Laboratory Duplicates

Laboratory duplicates are two aliquots of the same sample that are prepared, homogenized and analyzed in the same manner. (Note, proper sample homogenization is critical in producing meaningful results.) The precision of the sample preparation and analytical methods is determined by performing a laboratory duplicate analysis. Laboratory duplicates can be prepared in the field and submitted as blind samples, or

the laboratory can be requested to perform the laboratory duplicate analysis. In the case of laboratory prepared duplicates, the field sampling team must be sure to provide sufficient sample volume. Laboratory duplicates must be prepared and analyzed at a frequency of 1 per 20 samples or 1 per non-related concrete matrix, whichever is greater.

Calculate the RPD between the sample and its duplicate using Equation 1. The following general guidelines have been established for laboratory duplicate criteria:

- If both the original and laboratory duplicate values are ≥ PQL, then the control limit for RPD is ≤25%,
- If one or both values are < PQL, then do not assess the RPD.

If duplicate criteria are not met, then flag that target element with an "*" on the final report for both the original and duplicate samples. Report both the original and duplicate analyses; do not report the average.

9.4 Matrix Spike/Matrix Spike Duplicate Samples

Matrix spike/matrix spike duplicate samples (MS/MSDs) are two additional aliquots of a sample which are spiked with the appropriate compound(s) or analyte(s) of concern and then prepared and analyzed along with the original sample. (Note, proper sample homogenization, prior to spiking, is critical in producing meaningful results.) MS/MSDs help evaluate the effects of sample matrix on the analytical methods being used. The field sampling team must provide sufficient sample volume such that the field or fixed laboratory can prepare and analyze MS/MSDs at a frequency of 1 per 20 samples or 1 per non-related concrete matrix, whichever is greater.

Calculate the recovery of each matrix spike compound or analyte using Equation 2.

$$MSR = \frac{SSR - SR}{SA} x\ 100$$

Equation 2
Where,

MSR	=	Matrix Spike Recovery,	SA	=	Spike Added
SSR	=	Spiked Sample Result,	SR	=	Sample Result

Calculate the relative percent difference (RPD) between the recoveries of each compound or analyte in the matrix spike and matrix spike duplicate using Equation 3.

$$RPD = \frac{|MSR - MSRD|}{\frac{(MSR + MSRD)}{2}} x\ 100$$

Equation 3
Where,

MSR	=	Matrix Spike Recovery
MSRD	=	Matrix Spike Duplicate Recovery

9.5 Performance Evaluation Samples

In accordance with the EPA Region I Performance Evaluation Program Guidance, performance evaluation (PE) samples should be submitted for each type of analysis to be performed in the field or by the fixed laboratory performing full protocol EPA methods. PE samples provide information on the quality of the individual data packages. PE samples are certified standard reference materials (SRMs) from a source other than that used to calibrate the instrument. If both field and fixed laboratories are being used to analyze samples, at least one solid PE sample should undergo both field analysis and confirmatory full protocol EPA method analysis to facilitate data comparability. A copy of the certified values for the SRM must be submitted with the final data packages to facilitate data evaluation.

9.6 Data Verification and Validation

All field data and supporting information (including chain-of-custody) that is collected during a concrete sampling episode should be verified daily, by a person other than that performing the work, to check for possible errors.

During the project planning process, a plan for data validation should be established for all data, both for field and fixed laboratories. All data must be validated to assure that it is of a quality suitable to make project decisions. For help in developing a data validation program refer to Region I, EPA New England, Data Validation Functional Guidelines for Evaluating Environmental Analyses.

9.7 Audits

9.7.1 Internal Audits

As part of the Quality Assurance/Quality Control Program for any sampling project, a series of internal audit checks should be instituted to monitor and maintain the integrity of the sample collection process. Timely internal reviews will insure that proper sampling, decontamination, chain-of-custody and quality control procedures are being followed. Also, the internal audit review is there to monitor any corrective actions taken, and/or institute corrective actions that should have been taken and were not. All corrective actions taken must be documented in an appropriate logbook, and if any corrective actions impact the final data reported, then they must also be documented in the final report narrative. The results of all internal audits must be documented in a report, and copies of the report issued to the Project Manager and the Quality Assurance Manager. The original copy of any audit report must remain with the main project file and be available for review.

9.7.2 External Audits

The Agency reserves the right to perform periodic field audits to ensure compliance with this SOP.

10.0 References

1) Guidance for the Data Quality Objective Process, QA/G-4, EPA/600/R-96/055, September 1994.

2) EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations, QA/R-5, Interim Final, October 1997.

3) Guidance for the Preparation of Standard Operating Procedures for Quality-related Operations, QA/G-6, EPA/600/R-96/027, November 1995.

4) Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses, July 1996.

5) EPA Region I Performance Evaluation Program Guidance, July 1996.

6) U.S. EPA Code of Federal Regulations, 40 CFR, Part 136, Appendix B, Revised as of July 1995.

Appendix G

Reference Manuals for Field Measurement Instruments

1. HACH DR/820, DR/850, and DR/890 Portable Datalogging Colorimeter Instrument Manual
2. HACH DR/4000 Procedure – Sulfide
3. HACH DR/4000 Procedure – Nitrite
4. HACH DR/4000 Procedure – Iron, Ferrous
5. HACH DR/4000 Procedure – Manganese
6. HACH DR/4000 Procedure, Method 8038 – Nitrogen, Ammonia
7. HACH DR/4000 Procedure, Method 8155 – Nitrogen, Ammonia
8. HACH Water Analysis Handbook, Method 8205, Carbon Dioxide
9. HACH Water Analysis Handbook, Method 8203, Alkalinity
10. HACH Water Analysis Handbook, Method 8221, Alkalinity
11. HACH Digital Titrator Model 16900
12. Horiba Multi-Parameter Water Quality Monitoring System U-22XD Operation Manual
13. LaMotte 2020 Turbidimeter Instruction Manual
14. Using the MiniRae 2000 & ppbRAE PID
15. Tisch TE-6000 Series Operations Manual
16. Geometrics G-858 Magmapper Operation Manual
17. EM-31-MK2 Operating and Calibration Instructions
18. EM-31 Pro Operating Instructions – For Data Acquisition
19. EM61MK2 Operating Instructions
20. EM61MK2 Operating Instructions – For Data Acquisition
21. SIR System-2000 Operation Manual

48440-18

DR/820, DR/850, and DR/890

Portable Datalogging Colorimeter Instrument Manual

dd/dp 6/02/97 1ed
rev. 5, 8/99

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SAFETY PRECAUTIONS

Before attempting to unpack, set up or operate this instrument, please read this entire manual. Pay particular attention to all warnings, cautions and notes. Failure to do so could result in serious injury to the operator or damage to the equipment.

To ensure the protection provided by this equipment is not impaired, this equipment MUST NOT be installed or used in any manner other than that which is specified in this manual.

Use of Hazard Information

If multiple hazards exist, the signal word corresponding to the greatest hazard shall be used.

DANGER

Indicates either a potentially or an imminently hazardous situation which, if not avoided, could result in either death or serious injury

CAUTION

Indicates a potentially hazardous situation that may result in minor or moderate injury

NOTE

Information that requires special emphasis

Precautionary Labels

Please pay particular attention to labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed.

The DR/800 Series Colorimeters are Class 1 LED products. A Class 1 LED product has insufficient energy to be considered an eye hazard.

⚠ This symbol, if noted on the instrument, references the Instruction Manual for operational and/or safety information.

⚠ **Section *2.1 Battery Installation***

⚠ ***SECTION 4 CREATING USER-ENTERED PROGRAMS***

SPECIFICATIONS

Specifications subject to change without notice.

Wavelength Range(s):

- Model DR/890: 420, 520, 560, 610 nm
- Model DR/850: 520, 610 nm
- Model DR/820: 520 nm

Wavelength Accuracy: ±1 nm

Wavelength Selection: Automatic

Photometric Linearity: ±0.002 A (0-1 A)

Photometric Reproducibility: ±0.005 A (0-1 A)

Photometric Accuracy: ±0.005 A @1.0 ABS Nominal

Source Lamp: Light Emitting Diode (LED)

Detector: Silicon Photodiode

Data Readout: 4-digit LCD, 1.5-cm Character Height

Readout Modes: % Transmittance, Absorbance, Concentration

External Outputs: IR (Infrared to RS-232 Serial using the Data Transfer Adapter)

Battery Power: (4) AA alkaline cells

Instrument Dimensions: 23.6 x 8.7 x 4.7 cm (9.3 x 3.4 x 1.9 inches)

Instrument Weight: 470 g (1 lb.)

Photometric Range: 0-2 A

Stray Light: <1.0% at 400 nm

Battery Life: 6 months (typical)

Temperature Range:
Operating Range: 0 to 50 °C (32 to 122 °F)
Storage Range: -40 to 60 °C (- 40 to 140 °F)

Humidity: 90% at 50 °C

Environmental: Designed to meet IP67 Standard; dustproof and waterproof

OPERATION

DANGER

Handling chemical samples, standards, and reagents can be dangerous. Review the necessary Material Safety Data Sheets and become familiar with all safety procedures before handling any chemicals.

DANGER

La manipulation des échantillons chimiques, étalons et réactifs peut être dangereuse. Lire les Fiches de Données de Sécurité des Produits (FDSP) et se familiariser avec toutes les procédures de sécurité avant de manipuler tous les produits chimiques.

PELIGRO

La manipulación de muestras químicas, estándares y reactivos puede ser peligrosa. Revise las fichas de seguridad de materiales y familiarícese con los procedimientos de seguridad antes de manipular productos químicos.

GEFAHR

Das Arbeiten mit chemischen Proben, Standards und Reagenzien ist mit Gefahren verbunden. Es wird dem Benutzer dieser Produkte empfohlen, sich vor der Arbeit mit sicheren Verfahrensweisen und dem richtigen Gebrauch der Chemikalien vertraut zu machen und alle entsprechenden Materialsicherheitsdatenblätter aufmerksam zu lesen.

PERIGO

A manipulação de amostras, padrões e reagentes químicos pode ser perigosa. Reveja a folha dos dados de segurança do material e familiarize-se com todos os procedimentos de segurança antes de manipular quaisquer produtos químicos.

SECTION 1 GENERAL DESCRIPTION

1.1 Instrument Description

The Hach DR/800 Series Colorimeter shown in *Figure 1* is a microprocessor-controlled, LED-sourced filter photometer suitable for colorimetric testing in the laboratory or the field. The instrument is precalibrated for common colorimetric measurements and includes convenient calibration capability for user-entered and future Hach methods. Instrument features include:

- Test results are displayed in concentration, absorbance, or percent transmittance.
- Automatic wavelength selection and ranging in the preprogrammed parameters.
- Data storage and recall for datalogging in the field or laboratory.
- Conversion of results to alternate forms for many parameters (i.e., PO_4, P_2O_5, P).
- Reagent Blank Correction and Standard Adjust features may be used to compensate for lot-to-lot variations in reagents.
- Icon prompts displayed during testing.
- A built-in timer to monitor specific reaction times called for in the test procedures. Appropriate times are programmed into the calibration data for specific tests. The timer also can be used manually by the operator independent of the stored methods.
- IR output for RS232 interface capability allows an external printer or computer to interface with the colorimeter.
- Entry of user-entered methods or new Hach methods.
- Error signals for procedural or instrument troubleshooting.

The colorimeter operates on battery power. The instrument holds four AA-size alkaline dry cells (batteries supplied) that power the instrument for at least six (6) months. Optional rechargeable alkaline batteries are also available. The charger and optional rechargeable batteries must be purchased separately.

Figure 1 DR/800 Series Colorimeter Standard Package*

1.2 Unpacking the Instrument

Remove the instrument and accessories from the shipping container and inspect each item for any damage that may have occurred during shipping. Verify that all items listed on the packing slip are included. If any items are missing or damaged, please contact Hach Customer Service, Loveland, Colorado for instructions.

* Carrying Case may be ordered separately.

Hach's toll-free number for customers within the United States is 800-227-4224. For customers outside the United States, contact the Hach office or distributor serving you.

1.2.1 Standard Accessories

- Sample Cells — (2) round, with 10-mL, 20-mL, and 25-mL marks
- COD/TNT Adapter for use with 16-mm vials used in COD and Test 'N Tube methods.
- Batteries — (4) AA alkaline
- Documentation package — includes Instrument Manual and Procedures Manual.

In addition to these standard accessories, several other optional accessories are available from Hach Company (refer to *Replacement Parts and Accessories*).

1.2.2 Optional Accessories

- Immunoassay Tube Adapter
- Rechargeable Alkaline Batteries
- External Alkaline Battery Charger
- Data Transfer Adapter (for RS232 interface)
- HachLink™ Software
- Portable Printer
- Instrument case
- DR/Check™ ABS Standard

1.3 Description of the Keypad

Figure 2 shows the colorimeter's keypad. The description and function of each individual key is given in *Table 1*.

Figure 2 Keypad

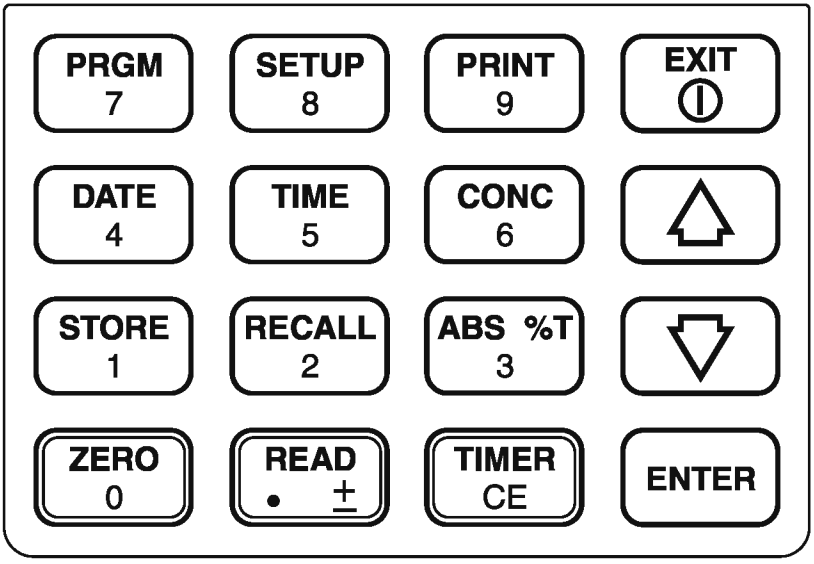


Table 1 Keys and Descriptions

KEY	DESCRIPTION
PRGM 7	Allows the user to select a program. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen.
SETUP 8	Accesses the SETUP menu (the SETUP icon illuminates in the upper left-hand corner of the display screen). The setup menu provides access to options such as reagent blank, standard adjust, user-entered programs, and instrument configurations. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen.
PRINT 9	Prints currently displayed data. In the RECALL menu, prints recalled data. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen.
EXIT ⏻	Use this key to turn the instrument on and, when the instrument is on and the EXIT icon is not illuminated, press this key to turn the instrument off. When the EXIT icon is illuminated at the base of the display screen, the **EXIT** key cancels the current entry or selection.

Table 1 Keys and Descriptions (Continued)

KEY	DESCRIPTION
DATE 4	Displays the current date. In the **RECALL** menu, displays the date the recalled sample was stored. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen. Used to set the current date from the **SETUP** menu.
TIME 5	Displays the current time. In the **RECALL** menu, displays the time the recalled sample was stored. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen. Used to set the current time from the **SETUP** menu.
CONC 6	When performing an analysis, this key displays the concentration value of the reading. Used as a toggle key to access alternate chemical forms, if available. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen.
△	Scrolls up through selected menus or stored data.
STORE 1	When performing an analysis, this key allows the user to store a current reading in one of 99 sample locations. The user can store the reading as numbers 1-99 by pressing **ENTER**. Use the up and down arrow keys to find unused storage numbers or use numeric keys to enter a sample number. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen.
RECALL 2	Begins the retrieval of stored sample readings (**RECALL** icon illuminates in the upper-left portion of the screen). Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen.
ABS %T 3	Toggles between displaying Absorbance and % Transmittance. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen.
▽	Scrolls down through selected menus or stored data.
ZERO 0	Zeros the instrument on the current sample blank. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen.
READ • ±	When the **READ** icon is illuminated at the base of the display screen, this key reads and displays the sample concentration. Also used as a numeric key function when the "#" icon is illuminated at the base of the display screen; the first press is a decimal, the second press toggles the value sign.
TIMER CE	If using a Hach-stored program, the **TIMER** key automatically sets the appropriate reaction time. If not in a Hach-stored program, the **TIMER** key allows the user to set a timer. When the "#" icon is illuminated at the base of the display screen**, CE** clears the most recent level of action (deletes the whole entry, not just the last number).
ENTER	Within a menu, selects the displayed menu item. During numeric entry, accepts the displayed value.

1.4 Display Screen in Function and Numeric Modes

The main display operates in two modes: function mode and numeric mode. The user does not select the mode, changeover is automatic depending on the options selected, where the user is in an analysis, and what information the instrument needs from the user.

The main display shows action icons (**ZERO** and **READ**) displayed below the horizontal line. This shows there are two available options to select (zero the instrument, or take a reading) at this point in the analysis.

The numeric mode is signified by the "#" icon illuminated below the horizontal line. In the numeric mode, some function keys act as numeric entry keys (corresponding to the number on the key).

1.5 Icon and Display Screen

Figure 3 shows the icons displayed by the DR/800 Series Colorimeters. *Table 2* provides a brief description of each display element.

Figure 3 Icon and Main Display Screen

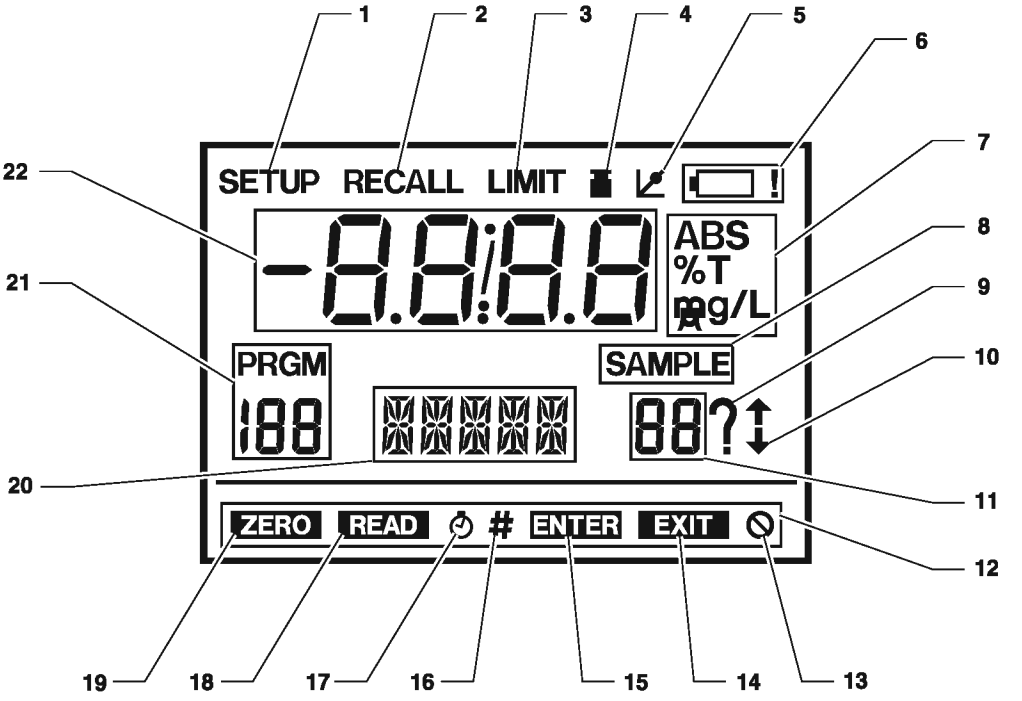


Table 2 Main Display Screen Icons

ITEM NO.	DEFINITION
1	Indicates the user is in the **SETUP** menu.
2	Indicates the user is in the **RECALL** menu.
3	The sample concentration exceeds the limits of the selected program.
4	Sample cell icon. Indicates a reagent blank adjustment is in use for the current program.
5	Standard adjust icon. Indicates a standard adjust is in use for the current program.
6	Indicates a low battery condition - replace the batteries as soon as possible.
7	These three icons follow the sample reading and represent either absorbance, percent transmittance, milligrams per liter, micrograms per liter, or grams per liter.
8	Illuminates whenever the numbers in the main display (22) or the sample display (11) refer to a sample number.
9	Indicates the instrument is waiting for information from the user.
10	Depending on the arrow(s) illuminated, these icons indicate the available scroll direction (using the **ARROW** keys) for accessing options.
11	In the RECALL menu or when storing data, these digits show the selected sample number.
12	Most icons displayed in this area are action icons. Action icons tell the user what actions are acceptable options during an analysis.
13	Indicates an invalid key press was made. This icon flashes briefly accompanied by a short beep.
14	Exit action icon - (when illuminated) tells the user that pressing the **EXIT** key to exit the current level of action is an acceptable option.
15	Enter action icon - (when illuminated) tells the user that pressing the **ENTER** key to confirm an action is an acceptable option.
16	Numeric entry action icon - (when illuminated) tells the user the numeric key pad is active.
17	Timer action icon - (when illuminated) tells the user that the instrument is presently running a timer. This icon will flash while the timer is counting.
18	Read action icon - (when illuminated) tells the user that pressing the **READ** key to read the sample cell is an acceptable option.
19	Zero action icon - (when illuminated) tells the user that pressing the **ZERO** key to zero the instrument on a sample cell is an acceptable option.
20	Depending on the currently active menu, the series of alphabetical letters displayed here gives information on a current reading, a stored reading, indicates the options available within a menu, or prompts the user for the next action.
21	Shows the active program number, (either a user-entered (101-110) or Hach-stored program (1-100). The program number is displayed immediately below the PRGM icon.
22	Depending on the currently active menu, the numbers displayed here represent either the sample reading, the clock timer, or the numeric characters entered by the user.

SECTION 2 INSTRUMENT SETUP

2.1 ⚠ Battery Installation

Power is supplied by four AA-sized alkaline batteries. Typically, a set of batteries provides approximately six months of operation. The colorimeter lamp is an LED and is on only long enough for the measurement sequence to take place (approximately 2 seconds).

The instrument will automatically shut off if no keystrokes are made for 15 minutes when in normal mode and four hours when in user-entry mode.

Figure 4 provides an exploded view of the battery installation. When replacing discharged batteries, always replace the complete set of four.

Hach recommends using alkaline batteries in this instrument. **Do not use rechargeable Nickel Cadmium (NiCad) batteries.** If rechargeable batteries are desired, rechargeable alkaline batteries are available from Hach.

The battery compartment is accessible from the underside of the instrument. Make sure the sample cell compartment is empty. Lay the instrument upside down on a padded surface, and install batteries as follows:

Note: *For performance reasons, never remove the battery cover from this product except when servicing the batteries.*

1. Disconnect the Data Transfer Adapter (if connected) from the instrument.
2. Loosen the two battery compartment screws and remove the battery compartment door as shown in *Figure 4*.
3. Install four AA alkaline batteries in the battery holder as shown in *Figure 4*. Match the polarities of the batteries with the polarity markings in the battery compartment.
4. Replace the battery compartment cover, tighten the screws, and return the instrument to the upright position.

DANGER ⚠
Use of nickel-cadmium batteries under a fault condition creates a potential fire hazard.

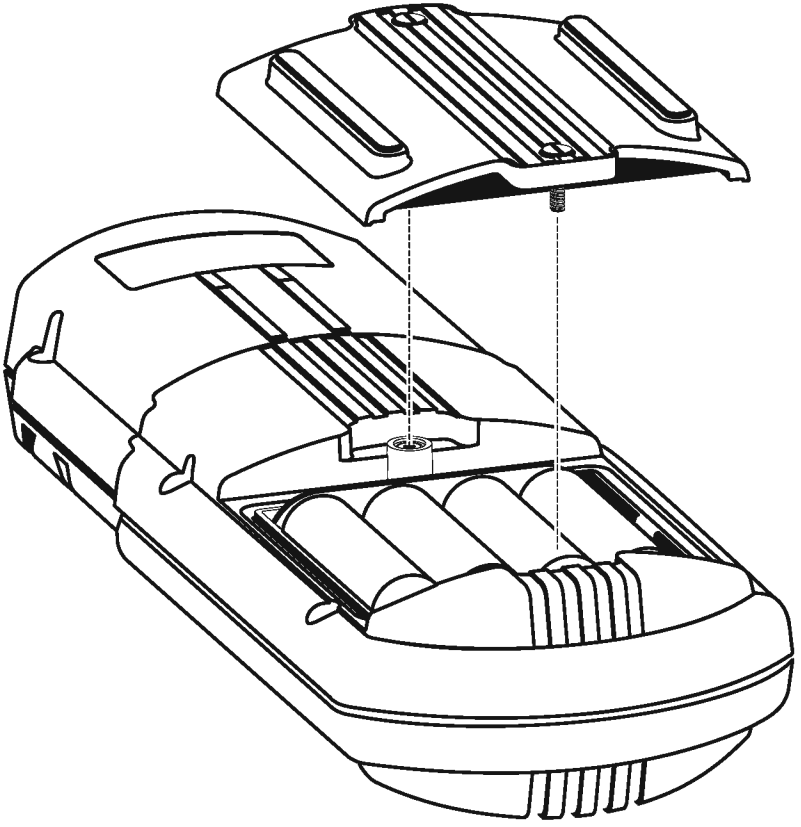
PELIGRO
La utilización de pilas de níquel-cadmio en condiciones de falla crea el riesgo de incendio.

PERIGRO
O uso de baterias de níquel-cádmio em condição de falha cria a possibilidade de incêndio.

DANGER
L'utilisation de batteries nickel-cadmium dans des conditions inappropriées crée un risque d'incendie.

GEFAHR
Unter einer Störungsbedingung stellt die Verwendung von Nickel-Kadmium-Batterien eine Feuergefahr dar.

Figure 4 Battery Installation



2.2 Turning the Instrument On

Once batteries are installed, turn the instrument on using the **EXIT/I/O**key (located on the top row, far-right column of the instrument keypad).

Press the key once to power-on the instrument. The display will show the software version number, then will default to the last used program number. The instrument is now ready for operation.

2.3 Setting the Date and Time

Setting the instrument's date and time allows sample readings to be stored and recalled with the proper date and time. Check the currently entered date or time by pressing the respective **DATE** or **TIME** key.

To set the date and time, continue with Section *2.3.1* or *2.3.2* below.

2.3.1 Entering the Correct Date

Check the current date by pressing the **DATE** key. If the date is incorrect, follow the procedure below to change it.

Enter the correct year, then the correct month and day as follows:

1. Press the **I/O** key to turn the instrument on.
2. Access the **SETUP** menu by pressing the **SETUP** key on the keypad. (The down **ARROW** icon on the right side of the display is shown.)
3. Press the down **ARROW** key until **DATE** is displayed.
4. Press the **ENTER** key to select the date option.
5. Four horizontal lines (showing available spaces for numeric entry) and **YEAR ?** will appear on the display. Enter the digits corresponding to the correct year using the numeric keypad. For instance, if the year is 1997, press **1 9 9 7** then the **ENTER** key.

   If an incorrect number is entered, press the **CE** key and re-enter the information.

Next, the instrument prompts for the month and day.

6. Enter the correct month and day using the numeric keypad. The month must be entered first, followed by the day. If an incorrect number is entered, press the **CE** key and re-enter the information.

Note: *When entering a one digit month or day, always press the* **ZERO** *key before the digit. For example: If the month and day to be entered is March 4, press* **0 3 0 4** *on the numeric keypad, then press the* **ENTER** *key to accept.*

7. Press the **ENTER** key to accept the new information. Press the **EXIT** key to return to the main menu

2.3.2 Entering the Correct Time

1. Press the **I/O** key to turn the instrument on.

2. Access the **SETUP** menu by pressing the **SETUP** key on the keypad. (The down **ARROW** icon on the right side of the display is shown.)

3. Press the down **ARROW** key until **TIME** is displayed.

4. Press the **ENTER** key to select the time option.

5. Enter the time in 24-hour (military) notation using the numeric keypad then press the **ENTER** key to accept the entry. For example, 9:00 a.m. is entered as **0 9 0 0 ENTER** and 2:00 p.m. is entered as **1 4 0 0 ENTER.** If an incorrect number is entered, press the **CE** key and re-enter the information.

6. The display returns to the setup menu. Press the **EXIT** key to return to the main menu.

2.4 Sample Cell Insertion

Wipe the sample cell with a lint-free cloth or tissue and insert the cellinto the sample cell compartment with the diamond-shaped marker toward the keypad.

Figure 5 Placing Samples in the Sample Cell Compartment

2.5 Sample Cell Adapter Installation

When installing an adapter into the sample cell compartment, insert the adapter into the cell compartment and rotate until it drops into the alignment slots. Finish installation by gently pushing down on the adapter until it snaps into position.

Place the appropriate vial or sample cell into the adapter - the vial or sample cell should fit well into the adapter. If it does not, double-check that the correct sample container (vial or sample cell) is being used and that the adapter is installed correctly. For a list of available adapters, refer to *Replacement Parts and Accessories*.

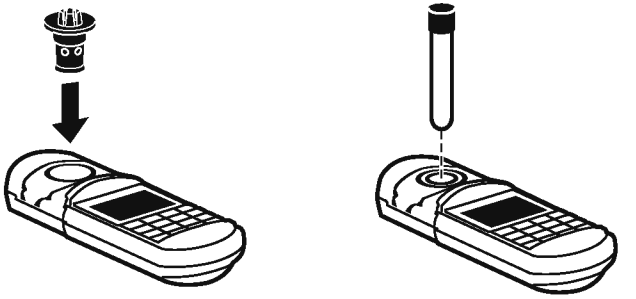
2.5.1 Using the 16-mm COD/Test ‘N Tube Vial Adapter

The methods for chemical oxygen demand (COD) and Test ‘N Tube (TNT) determinations in the colorimeter procedures manual use 16-mm vials as the sample cell for the colorimetric measurement. This adapter also holds a standard 16-mm test tube.

Place the COD/TNT Adapter in the instrument's sample cell compartment as instructed in Section *2.5*, above. Place the vial into the COD/TNT Adapter (see *Figure 6*).

Always place the instrument cap over the adapter when measuring in bright sunlight (see *Figure 8*).

Figure 6 Installing the COD/TNT Adapter



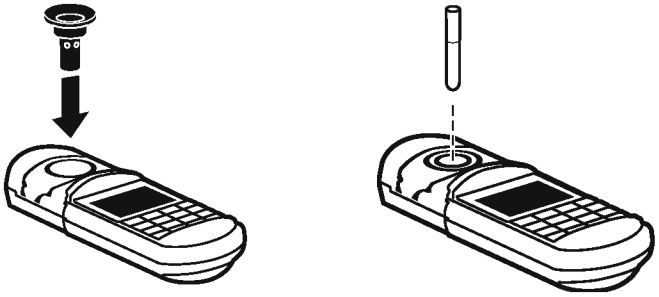
2.5.2 Using the Immunoassay Tube Adapter

Immunoassay methods develop and read the color in special antibody coated tubes. The instrument can read immunoassay results with the aid of the adapter.

Place the Immunoassay Tube Adapter in the instrument's sample cell compartment as instructed in section *2.5*, above. Place the tube into the adapter after it is properly installed in the cell compartment (see *Figure 7*).

Always place the instrument cap over the adapter when measuring in bright sunlight (see *Figure 8*).

Figure 7 Installing the Immunoassay Tube Adapter

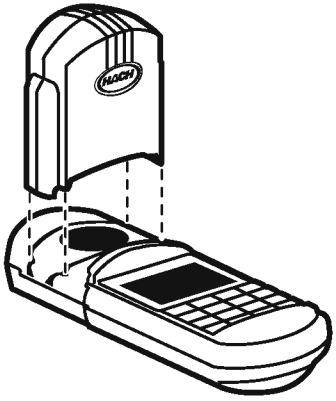


2.6 Using the Instrument Cap as A Light Shield

The colorimeter cap is removable (by sliding it away from the keypad) to expose the sample cell compartment. The instrument cap also functions as a light shield. Samples may be analyzed without the light shield in place but using the light shield provides a good seal against stray light and contributes to more accurate results. Use of the light shield is especially important when performing an analysis in bright light or direct sunlight.

To use the instrument cover as a light shield during measurements, place the cap over the sample cell, into the grooved marks on the instrument. See *Figure 8*.

Figure 8 Installing the Light Shield



SECTION 3 INSTRUMENT OPERATION

3.1 Menus

The instrument has two important menus which allow access to different options. The menus are:

- Setup Menu
- Recall Menu

Once the user has selected the desired menu, the arrow icons illuminate on the main display screen. The arrows indicate that additional options are available in this menu. Press the up or down **ARROW** key (whichever arrow is illuminated) to scroll until the desired option is displayed. A press of the **ENTER** key at this time selects the displayed option.

When choosing options from menus, the up or down **ARROW** keys, **ENTER,** and **EXIT** keys help navigate between menus and within menu options. Use the **ENTER** key to select a menu option. Press **ENTER** again to accept a new setting. Pressing the **EXIT** key leaves a menu or leaves the displayed item unchanged.

3.1.1 Setup Menu

Enter the **Setup Menu** from the **Main Menu** by pressing the **SETUP** key.

Refer to the arrow icons on the main display for an indication of which key (up **ARROW** or down **ARROW**) to press on the keypad - the direction of the illuminated icon on the main display indicates the available scrolling direction. The up and down **ARROW** (scroll) keys move from one menu option to the next.

Example: when the down arrow icon is illuminated on the display screen, the user only has the option to press the down **ARROW** key to move from one option to the next. Once the user scrolls down, the down arrow icon changes to a dual-direction arrow icon (up and down arrows) until the user reaches the last menu option available in that menu.

The following instrument operating features are available in the **Setup** menu

- **BLANK** - Used to compensate for color contributed by the reagents in a reagent blank. Readjust for each new lot of

reagents. Press the **ENTER** key to activate this option. The default setting is off. Chemistries which zero on a reagent blank do not have this option available.

- **STD** - Standard Adjust option allows for entry of the value of the prepared standard. Press the **ENTER** key to activate this option. The default setting is off.

Note: *The BLANK and/or STD options may or may not be available, depending on the selected Hach program; the BLANK and STD options are always available for user-entered programs.*

- **PRINT (ALL)** - Prints all stored data to a printer or downloads it to a personal computer. The information printed includes: sample concentration reading, date of sample, time of sample, units, sample number, program number, Absorbance, and %T. Refer to Section *SECTION 6* for detailed printing information and to *Figure 11* for an example of a printout. Press the **ENTER** key to activate this option.

- **USER** - Allows access to the User-Entered Program Menu. Press the **ENTER** key to activate this option. See *CREATING USER-ENTERED PROGRAMS* on page *35* for more information.

- **DATE** - Allows the user to set the date. Press the **ENTER** key to activate this option. See Section *2.3.1* for more information.

- **TIME** - Allows the user to set the time. Press the **ENTER** key to activate this option. See Section *2.3.2* for more information.

- **ERASE (ALL)** - This clears all the data previously stored in memory. Press the **ENTER** key to activate this option.

3.1.2 Recall Menu

The recall menu allows access to stored data. Complete information and instructions for the use of this menu is presented in *SECTION 5 DATA RECALL AND STORAGE*.

3.2 Performing an Analysis

The procedures manual provides illustrated, step-by-step procedures for performing all the factory-entered methods. This instrument manual has supplemental information on how the instrument performs the necessary functions, and how to use the special operating features. Once you are familiar with the

instrument, the instructions in the procedure manual should be sufficient to analyze your samples.

Colorimetric testing with preprogrammed calibrations can be divided into four general phases:

1. Colorimeter setup
2. Sample preparation
3. Zeroing the instrument
4. Measuring the prepared sample

The following sections describe each phase in detail.

3.2.1 Colorimeter Setup for Sample Analysis

The colorimeter setup using a Hach program begins by selecting the desired program number. Programs numbers can be found in the individual procedure. (See the DR/800 Series Procedures manual supplied with your instrument.) Prompting icons will appear to indicate which keys are acceptable for the user to select. After turning the instrument on, the main display shows information from the last program used before the instrument was turned off.

If a different program is desired, press the **PRGM** key and enter the desired program number with the numeric keypad. The instrument will recall that program.

If the number selected is not valid, an error signal sounds and the display momentarily flashes an error icon. The display returns to the prompt for the program number. Re-enter the correct program number. Only select chemistries are available on the DR/820 and DR/850. See *APPENDIX A AVAILABLE PARAMETERS AND RANGES* on page *59*.

When the program number has been successfully entered, the display immediately prompts the user to zero the instrument by illuminating the **ZERO** action icon.

3.2.2 Sample Preparation

For colorimetric tests, sample preparation is next. The zero solution (or blank) and sample are usually prepared at this time. Generally, sample preparation consists of adding the contents of a premeasured reagent pillow to a small volume of sample. Follow the instructions in the procedure specific to your analysis.

It is important to observe the waiting period specified in the test procedure to ensure the color from the reaction of the reagent(s) with the target analyte develops fully. Many procedures also give a maximum time limit after which the color may begin to fade.

The instrument has method-specific timers for color development times pre-programmed into the software. The user is notified when the time has elapsed by a series of short beeps.

3.2.3 Zeroing the Colorimeter

The instrument must be zeroed for each test or series of tests to establish a zero reference for the measurement. This is done by placing a solution recognized as the blank solution in the cell holder, covering the sample with the instrument cap, and pressing the **ZERO** key. The next prompt will display zeros and illuminate the **READ** action icon. The instrument is now ready to take the first sample reading.

Note: *Once the zero reference point has been established, several samples can be measured consecutively by placing each of them into the cell holder and pressing the* **READ** *key. The instrument can be re-zeroed at any time by placing the zero solution (blank) into the instrument and pressing the* **ZERO** *key.*

3.2.4 Measuring the Prepared Sample

When ready to take the reading, place the prepared sample in the sample compartment. For best results orient the sample cell consistently for each measurement; see *Figure 5* on page *21*. Place the instrument cap (light shield) over the sample cell and press the **READ** key. After a brief pause, the results will be displayed.

Toggle between absorbance or percent transmittance values by successive presses of the **ABS %T** key. Press the **CONC** key to restore the concentration display. Successive presses of the **CONC** key toggles between alternate forms, if any. See Appendix A for currently available chemistries and their alternate forms.

3.2.5 Alternate Chemical Forms

Many Hach programs provide alternate chemical forms for the measured parameter. Press the **CONC** key to scroll through these alternate forms after the measurement is displayed. Each press of the **CONC** key takes the user to the next alternate chemical form. For example: In Program #1, mg/L Al may also be displayed as mg/L Al_2O_3. If alternate forms are not available, the instrument returns to its original form and reading.

3.2.6 Using the Timer

Many Hach test methods use one or more timers which are pre-programmed into the DR/800 Series Colorimeters. When the procedure instructs you to, press the **TIMER** key to display a timer interval. Press **ENTER** to start the timer count-down. Several beeps will sound at the end of a timer interval. If the method requires additional timers, the instrument will automatically display the next timer when the first timer elapses. Press **ENTER** to start the next timer.

To zero the instrument on the blank while the timer is running, press the **EXIT** key. The timer icon will continue to flash, indicating the timer is running. Press **ZERO**, or perform other available functions within the method (such as blank correction) while the timer is running. To return to the timer display, press the **TIMER** key.

3.2.6.1 Using the Timer in Manual Mode

The manual timer function allows the operator to use the timer independently from the method timer. Make sure the instrument is not in numeric entry mode and activate the timer with a press of the **TIMER** key. If using a pre-programmed timer, press the **TIMER** key again.

The "#" action icon is illuminated, to indicate that the numeric keypad is active. Enter the desired time using the numeric keypad. For example, to enter 2 minutes, press **2 0 0,** then **ENTER.** To enter 12 minutes, press **1 2 0 0,** then **ENTER**. The display will momentarily show the entered time, then the timer countdown will begin. The display will show the remaining time. At the end of the elapsed time, the instrument sounds five beeps.

3.2.6.2 Stopping the Timer

Stop the timer at any point in the countdown by pressing the **ENTER** key. If a pre-programmed timer was in use, the full timer period will be displayed. Press the **ENTER** key again to resume count down. If a manual timer was in use, the display for entering a new length of time will be shown, see Section *3.2.6.1 Using the Timer in Manual Mode*. Press **EXIT** to leave the timer mode.

3.3 Reagent Blank Correction

The Reagent Blank Correction can be used with some of the factory-entered methods. It subtracts the color absorbed when running the test with deionized water instead of sample. The blank value is subtracted from every result to correct for any background color due to reagents.

When using the Reagent Blank Correction feature, the blank correction should be entered before the Standard Adjust feature is used.

To enter a programmed correction for the reagent blank:

1. Run the test using deionized water with each new lot of reagents.
2. Press **READ** to obtain the blank value; record the value for use in step *4.*.
3. Press **SETUP**, scroll to **BLANK** and press **ENTER**. The display will show **BLANK?**.
4. Enter the blank value obtained in step *2.*.
5. Press **ENTER** to accept the value as the blank to be subtracted from each reading.
6. The display will show 0.00 mg/L (resolution and units vary with the method) and the sample cell icon will be displayed, indicating that the reagent blank feature is enabled and the blank value will be subtracted from each reading. Repeat the reagent blank adjust for each new lot of reagents.

Note: *After entering a reagent blank adjust, the display may flash "limit" when zeroing if the sample used for zeroing has a lower absorbance value than the reagent blank.*

To disable the Reagent Blank adjust feature, press **SETUP**, scroll to **BLANK** and press **ENTER** twice. The concentration readings will be displayed without subtracting the blank. The sample cell icon will no longer appear in the display.

Do not attempt to use the Reagent Blank Adjust feature if the procedure uses a reagent blank for zeroing.

3.4 Adjusting the Standard Curve

The DR/890 Colorimeter has over 90 Hach Programs permanently installed in memory (other models have fewer programs). A program usually includes a preprogrammed calibration curve. Each curve is the result of an extensive calibration performed under ideal conditions and is normally adequate for most testing. Deviations from the curve can occur from using compromised testing reagents, defective sample cells, incorrect test procedure, incorrect technique, or other correctable causes. Interfering substances or other causes may be beyond the analyst's control.

In some situations, using the preprogrammed curve may not be convenient:

- Running tests where frequent calibration curve checks are required.
- Testing samples which give a consistent test interference.

Consider the following before adjusting the calibration curve:

1. Will future test results be improved by adjusting the curve?
2. Are interfering substances consistent in all the samples that you will test?

Any precision and test range information provided with the procedure may not apply to an adjusted curve calibration.

You can adjust many of the calibration curves by following the steps found in the test procedures. Working carefully is important. After the adjustment, it is wise to run standard solutions of several concentrations to make sure the adjusted curve is satisfactory. Perform standard additions on typical samples to help determine if the adjusted curve is acceptable.

Think of the standard adjust measurement as a two-step process. First, the instrument measures the sample using the preprogrammed calibration. Second, it multiplies this measurement by an adjustment factor. The factor is the same for all concentrations. The instrument will remember the factor indefinitely and will display the standard adjustment icon when it is used.

Adjust the calibration curve using the reading obtained with a Hach Standard Solution or carefully prepared standard made from a concentrated Hach Standard Solution. It is important to adjust the curve in the correct concentration range. For most purposes, Hach recommends adjusting the curve using a standard concentration that is 70 to 85% of the maximum concentration range of the test.

For example, the Hach preprogrammed method for fluoride has a range of 0-2.0 mg/L F. To adjust the calibration curve, use a standard with a concentration between 1.4-1.6 mg/L. Hach provides a 1.60 mg/L Fluoride Standard Solution (80% of the full range). This is a convenient standard to use for adjusting the calibration curve.

If the range of all your samples is known to be below a concentration that is less than 50% of the full range (50% of 2.0 is 1.0 mg/L), then adjust the standard curve with a standard that is within that range.

For example, if all the samples contain 0.6-0.9 mg/L F, you may use a 1.00 mg/L fluoride standard to adjust the curve. You may use the 1.00 mg/L standard because it is closer to the sample range you are working with.

If you are using a Reagent Blank Correction, the blank correction should be entered before the standard curve is adjusted.

To adjust the standard curve:

1. Prepare the standard.

2. Use the standard as the sample in the procedure.

3. When the reading for the standard is obtained, press **SETUP**.

4. Use the **ARROW** keys to scroll to the "**STD**" setup option.

5. Press **ENTER** to activate the standard adjust option.

6. Enter the concentration of the standard used.

7. Press **ENTER**. The standard adjust icon will be displayed, indicating that the curve has been adjusted with the standard.

Note: *If the attempted correction is outside the allowable adjustment limit, the instrument will beep and flash the error icon and the operation will not be allowed.*

To eliminate the standard curve adjustment:

1. Press the **PRGM** key.

2. Enter the stored-program number and press **ENTER**.

3. Press the **SETUP** key

4. Press an **ARROW** key to display **STD**.

Note: *On will be displayed if an adjustment is in use.*

5. Press **ENTER** twice.

3.5 Using a Programmed Method

Hach programmed and user-entered program options are available on this instrument. The Procedures Manual supplied at the time of purchase contains all currently available Hach-programmed methods. Up to ten user-programmed methods may be entered into the instrument. See *CREATING USER-ENTERED PROGRAMS* on page *35* for instructions for this function. *Table 3* shows the components of typical factory programmed test method.

Table 3

Step	Action/Keystroke	Display
1. Turn power on.	Press the **EXIT/I/O** key.	The instrument defaults to and displays the initial screen of the last program used. EXAMPLE: If program 20 was the last program in use, the instrument will automatically recall program 20.
2. Select the Program number to be used.	Press the **PGRM** key, then enter the program number and press the **ENTER** key.	After the **PGRM** key is pressed, a blinking cursor appears with a question mark. Enter the desired program number. Press **ENTER** to confirm this action and recall the desired program number.
3. As needed, set, then start the **TIMER**.	Press the **TIMER** key. In a Hach-stored program, the timer automatically defaults to the appropriate reaction time. Press **ENTER** to start the timer.	The entered or programmed reaction time will display and count down to zero.
4. ZERO the instrument using the sample blank.	Insert blank and press **ZERO.**	After the **ZERO** key is pressed, the instrument zeros on the sample cell.
5. Obtain reading in concentration, absorbance, or % transmittance.	Place the prepared sample into the cell holder. Press **READ**.	The instrument reads the sample and displays the results.

3.6 Quality Assurance

Verify the performance of your instrument in seconds using Hach DR/Check™ ABS Secondary Standards (Cat. No. 27639-00). These gel standards provide a measure of instrument absorbance for use anywhere, anytime, as often as laboratory quality assurance procedures suggest. The kit includes a blank and one standard each of a low-, mid-, and high range absorbance value from 0 to 2 ABS, for use with any DR/800 Series Colorimeter.

SECTION 4 CREATING USER-ENTERED PROGRAMS

DANGER
This instrument is not intended for use with flammable samples or those containing hydrocarbons.

PELIGRO
Este instrumento no está destinado para uso con muestras inflamables o que contengan hidrocarburos.

PERIGO
Este instrumento não é feito com o fim de ser empregado com amostras inflamáveis ou aquelas que contêm hidrocarbonetos.

DANGER
Cet instrument n'est pas conçu pour une utilisation avec des échantillons inflammables ou des échantillons contenant des hydrocarbures.

GEFAHR
Dieses Gerät darf nicht für Tests mit brennbaren Proben oder Proben, die Kohlenwasserstoffe enthalten, benutzt werden.

The DR/800 Series Colorimeters can store the calibration information needed to read prepared samples from up to five different user-entered programs. To create a new, user-entered program, you will need a blank and prepared standards or the correct absorbance readings for each standard. The prepared standards are made with standard solutions of the parameter (i.e. analyte). Up to twelve concentrations of standards, including a zero concentration standard, may be used.

The absorbances of the prepared standards must be different from one another. If the colorimeter detects a duplicate, it will beep and ignore the latest reading.

Using a previously entered method's program number erases all the previously entered information stored under that program number.

While creating a user-entered program, the colorimeter remains on for four hours following any keypress. If more than four hours pass between keypresses, the instrument will power down. All data which was entered, but not yet stored, will be deleted. The user-entered program must be re-entered from the beginning.

4.1 User-Entered Programs

The instrument allows storage of up to five user-entered programs (101-105) and up to 113 Hach programs.
A minimum of two data points are required for the instrument to recognize and accept a user-entered program.

- Program numbers 101 through 105 are reserved for storing user-entered programs.
- The maximum number of data points that can be entered for a method is 12. After the twelfth standard (1 through 12) is accepted, the instrument stores the method and will not accept any more data, but will allow the user to review the data already entered.

Before entering a calibration, determine the optimum wavelength, timing sequences (if any), and the workable range of the method.

4.2 Calibration Curves

Calibration curves may have positive or negative slopes, but they must be based on absorbance (% transmittance not allowed) and must pass through the origin that represents zero concentration.

It is important that the standards adequately describe the curve over the range of interest. Because this is largely dependent on the shape of the curve, it may be necessary to prepare a preliminary curve using extra data points to help select the appropriate standards.

If the curve is linear, only two concentration data points are needed. For example, standards with a zero absorbance and a standard with 1.000 absorbance are appropriate. If the curve is nonlinear, additional data points are needed to achieve good accuracy. Up to 12 data points can be entered for a single calibration curve.

4.3 User-entered Program Information for Bleaching Chemistries

Although the majority of colorimetric test procedures produce a higher absorbance (i.e. deeper color) as the concentration of the parameter being measured increases, some tests do the opposite. These bleaching chemistries (fluoride is one example) produce a lighter color at increasing concentrations. The zero concentration

standard is usually produced by combining deionized water with the reagents. Commonly this solution is used to zero the instrument as in Step *step 14* of *Section 4.4 Creating a New User-entered Program*.

Once the zero is entered, the prepared standards must be read from lightest to darkest. In the case of bleaching chemistries, the absorbance values reported by the colorimeter may be negative.

Even when your test produces a lower absorbance (lighter color) with increasing concentration, the prepared standards must be read by the colorimeter in the order of increasing absorbance (i.e., from colorless or the palest color, to the deepest color). The instrument will not accept standards read out of order.

4.4 Creating a New User-entered Program

Use the step-by-step instructions below to enter a new user-entered program into instrument memory. Terminate at any point (before the program is stored) by pressing the **EXIT** key until the display is blank. The colorimeter will not retain any of the entered data.

1. Press the **I/O** key to turn on the instrument.
2. Press the **SETUP** key. The display will show **SETUP** in the upper-left and the down-arrow icon in the lower-right. Available action functions are also shown.
3. Press the down **ARROW** key until **USER** is displayed.
4. Press the up **ARROW** key if the display goes past **USER**.
5. Press the **ENTER** key. Four horizontal lines (numeric entry display) will be displayed.
6. Select a program number from 101 through 105 by pressing the corresponding digit key. The number will appear in the display.

Note: *Press* **CE** *to correct errors.*

7. Press **ENTER**. A wavelength and **nm** will be displayed.

- If the wavelength is correct as displayed, skip to Step *step 8*.

- Some instrument models can use different wavelengths. If a different wavelength is preferred, proceed as follows:

a. Press **ENTER**. A flashing question mark will be displayed in the lower-right corner.

b. Press either **ARROW** key until the preferred wavelength is displayed.

c. Press **ENTER** to accept the displayed wavelength. The down-arrow icon will be displayed.

8. Press the down **ARROW** key to move to the **RES** (resolution) option. One to four zeros, a decimal point if needed, and the units of concentration may be modified here.

- If the displayed resolution and units are correct, skip to step *step 9*.

- If the displayed resolution or units are incorrect for your test, proceed with the following:

a. Press **ENTER**. A flashing question mark will be displayed.

b. Press either **ARROW** key until the preferred resolution and concentration units are displayed. The available options are:

0.000	0.00	0.0	0
0.000 µg/L	0.00 µg/L	0.0 µg/L	0 µg/L
0.000 mg/L	0.00 mg/L	0.0 mg/L	0 mg/L
0.000 g/L	0.00 g/L	0.0 g/L	0 g/L

c. Press **ENTER**. The question mark will disappear.

9. Press the down **ARROW** key to scroll to **STD**. **STD** and the number of the standard (i.e., 1 is shown for the first standard, 2 for the second, etc.) will be shown on the lower portion of the display.

10. Press **ENTER**. Four horizontal lines (denoting numeric entry) will be displayed.

11. Enter the standard's concentration, using the numeric entry keys (the # icon will be illuminated on the display).

Note: *Press the* **CE** *key to correct errors.*

12. Press the **ENTER** key. The concentration will be displayed.

Note: *A beep means that the concentration is a duplicate of a previous standard or the concentration is too high for the selected resolution. Repeat step step 11 with a different concentration and continue.*

13. Press the down **ARROW** key. **ABS** will be displayed followed by the number of the standard.

14. The colorimeter requires one zero be entered in this procedure; the **ZERO** action icon will appear in the lower portion of the display. Place a blank into the cell holder and press the **ZERO** key. Four horizontal lines will appear, then disappear, across the display. The **READ** action icon will appear in the lower portion of the display.

Note: *If necessary, the colorimeter can be re-zeroed. The most recently entered zero will be used for subsequent readings.*

15. Prepare the standards using the same reagents and procedure used to test samples.

16. Place the prepared standard into the cell holder.

17. Press the **READ** key. An absorbance value will be displayed.

Note: *Or, press the* **ENTER** *key to input an absorbance value or change the value read by the instrument. Use the numeric keys to enter the value then press the* **ENTER** *key.*

Note: *A beep indicates that the absorbance is a duplicate of a previously entered standard or that it falls between two previous standards. Repeat steps step 15 through 17. with the correct standard, or press the up* **ARROW** *key and repeat steps 9. through 17. with a correct, prepared standard and blank.*

18. Press the down **ARROW** key to advance to the next standard.

19. Repeat steps *step 9* through *step 18* for all remaining standards.

20. Press the **EXIT** key once. **STORE ?** will be displayed.

21. Press the **ENTER** key to store the new method in the instrument's memory.

4.5 Reviewing and Editing User-Entered Programs

Note: *When a user-entered program is edited and stored, all stored data associated with that program is erased.*

All method information previously stored by the operator can be reviewed and changed to add, delete, or modify data points. At any point during the editing function, the operator can terminate the procedure and exit by pressing the **EXIT** key. No changes to the program will occur.

Because the standards must be read in the order of increasing absorbancy, data points may not be inserted into the middle of an existing user-entered program.

To review and edit previously stored user-entered programs:

1. Press the **I/O** key to turn the instrument on.

2. Press the **SETUP** key.

3. Scroll to the **USER** option and press **ENTER**.

4. Enter the program number of the method to review or edit and press the **ENTER** key.

5. Scroll through the calibration information using the **ARROW** keys. To avoid making changes, press the **EXIT** key.

6. To edit the data shown on the display, press **ENTER**. Make necessary changes, then press the **ENTER** key to return to reviewing the data.

7. Press **EXIT** once. **STORE?** will be displayed.

8. Press **ENTER** to store the program.

4.6 Erasing User-entered Programs

Note: *When a user-entered program is erased, all stored data associated with that program is also erased.*

User-entered programs are automatically deleted when another user-entered program is entered and stored in the previously entered method's storage number (101-105). They also may be erased from the instrument memory as follows:

1. Press the **I/O** key to turn the instrument on.
2. Press the **SETUP** key.
3. Scroll to the **USER** option and press **ENTER**.
4. Enter the program number of the method to be erased and then press **ENTER**.
5. Scroll to the concentration data for STD 1 using the down **ARROW** key. Press **ENTER**.
6. Press **CE**. Press **ENTER**.
7. Press the **EXIT** key. **ERASE?** will be displayed.
8. Press the **ENTER** key to erase the method or the **EXIT** key to retain it in memory.

To store sample data, press **STORE** after the sample measurement is displayed. Data must be stored if you wish to recall it later for review, downloading or printing. The following information is stored for each sample:

- instrument model
- instrument serial number
- chemical form
- concentration
- units
- absorbance
- %T
- date
- time
- sample number
- program number

After the **STORE** key is pressed, a flashing question mark icon is shown in the lower-right portion of the display. In the center of the display, the next available storage number will appear. If this storage location is acceptable, press **ENTER** to accept it.

To select an empty storage number (between 1 and 99), use the **ARROW** keys to scroll to the desired number or enter the desired number with the numeric keys. Press **ENTER** to accept. The instrument will store the data, then revert back to the measurement display.

5.1 Recalling Data

To recall data stored in the colorimeter, press the **RECALL** key.

Use the **ARROW** keys to scroll through the stored data. Only data numbers containing stored sample reading data (of the available storage numbers 1-99) are displayed in the RECALL menu. For

example, if the user has stored data into storage numbers 6, 10 and 15, those are the only accessible numbers in the Recall option. Available storage numbers are not shown as a Recall option because no data has been stored for recall purposes.

When a number of sample readings have been stored and a specific reading must be recalled, proceed as follows:

1. Press the **I/O** key to turn the colorimeter on.
2. Press the **RECALL** key to access the **RECALL** Menu.
3. A beep indicates that no data is presently stored.
4. Press the number key(s) or either **ARROW** key on the keypad to scroll to the desired sample number.
5. Press the **ENTER** key. The stored reading will be displayed.
6. A beep indicates that no data is stored as that sample number.
7. While the stored reading is displayed, press the **DATE** key or the **TIME** key to display the date or time the reading was stored. Press the **CONC** key to display the concentration data.
8. If other stored data is desired, press either **ARROW** key until the data is displayed.
9. Press **EXIT** to terminate data recall.

5.2 Erasing All Stored Data

Stored data can be erased and the memory of the instrument cleared using the procedure that follows.

1. Press the **I/O** key to turn the colorimeter on.
2. Press the **SETUP** key to enter the **SETUP** menu.
3. Scroll using the down **ARROW** key until **ERASE** and **ALL** appears on the display.
4. Press the **ENTER** key to confirm this selection with the instrument.

A flashing question mark icon will appear in the lower-right portion of the screen as an additional step to avoid erasing all data if the choice was made erroneously.

5. Confirm this action by pressing the **ENTER** key or, if this is not the desired action, press the **EXIT** key.

After the **ENTER** key is pressed, the instrument automatically erases all stored data and returns to the last used program.

SECTION 6 PRINTING AND DATA TRANSFER

6.1 Data Transfer Adapter Basics

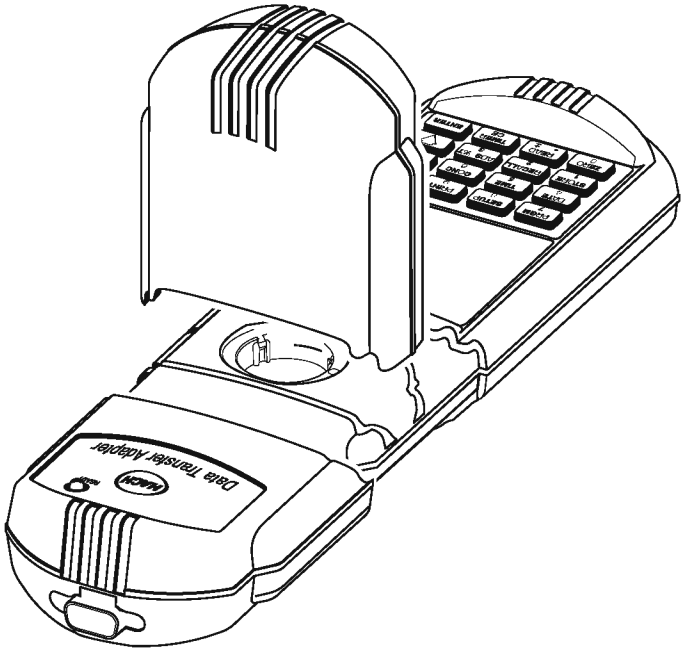
The optional Data Transfer Adapter (DTA) utilizes infra-red technology to receive data from the DR/800 Series Colorimeter and then transfer the signal into RS232 format. The DTA then sends the RS232 signal to a printer or personal computer.

The sleeve design makes the adapter compact, easy to use, and robust. Samples may be tested while the adapter is in place and the information may be immediately printed or downloaded to a computer. Data stored in the instrument memory may also be printed or downloaded at any time.

6.1.1 Attaching the Data Transfer Adapter

The Data Transfer Adapter is designed to fit on the instrument in the same way the instrument cap does. To install the DTA, simply remove the instrument cap, then slide the DTA onto the colorimeter body until it snaps into place. The DTA design allows the instrument cap to be used as a light shield. See *Figure 9 Installing the Data Transfer Adapter*.

Figure 9 Installing the Data Transfer Adapter



6.2 RS232 Connections

The RS232 receptacle on the Data Transfer Adapter connects with a 9-pin Sub-D connector (see *Figure 10 RS232 Connection*). A suitable RS232 cable is listed under Optional Accessories in *REPLACEMENT PARTS* on page *69*.

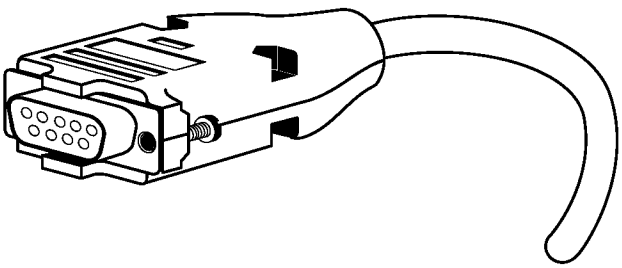
The RS232 interface output is an eight-bit data word plus one stop bit and no parity with a baud rate of 1200. It can communicate with either a serial printer or a serial communication port on a computer.

Press the **PRINT** key to send data to the printer or computer. See Section *6.3 Sending Data to a Printer or Computer* for instructions.

With the use of a serial-to-parallel converter, the data string transmitted from the colorimeter prints on any compatible parallel printer of the type normally used with IBM compatible applications.

All RS232 connections are made using the serial I/O port on the DTA. This port uses an industry standard 9-pin connector. See *Figure 10 RS232 Connection*.

Figure 10 RS232 Connection



Note: *For optimum performance and ESD protection, use a five-conductor shielded cable. Use a metal shell for the printer or CRT terminal connector, and connect the shield of the cable to the metal shell and to the sleeve (signal ground) of the RS232 plug.*

6.2.1 Setup and Use of the Printer

Follow the manufacturer's instructions when configuring the printer for compatibility with the colorimeter.

Pressing **PRINT** manually starts the printing, and pressing the **EXIT** key stops the printing (refer to Section *6.3 Sending Data to a Printer or Computer).*

Connect the DTA to a printer using the printer interface cable listed in *REPLACEMENT PARTS* on page *69*. The cable provides a direct link between the instrument and the 9-pin connector used for the serial port on most serial printers.

Table 4 and *Table 5* show the proper pin connections for 9-pin computer cables and for 25-pin printer cables. Use of cables that do not match the pin information given may cause undesirable operation.

Table 4 Standard 9-pin to 9-pin Computer Cable

DR/800 Series 9-pin Connector Socket		Computer 9-pin D Connector, plug	
Pin	**Signal Name**	**Pin**	**Signal Name**
2	RXD	3	TXD
3	TXD	2	RXD
4	DTR	no connection	—
5	GND	5	GND
6	DSR	no connection	—
7	RTS	8	CTS
8	CTS	7	RTS

Table 5 Standard 9-pin to 25-pin Printer Cable

DR/800 Series 9-pin Connector Socket		Computer 9-pin D Connector, plug	
Pin	**Signal Name**	**Pin**	**Signal Name**
2	RXD	no connection	—
3	TXD	3	RXD
4	DTR	no connection	—
5	GND	7	GND

Table 5 Standard 9-pin to 25-pin Printer Cable

DR/800 Series 9-pin Connector Socket		Computer 9-pin D Connector, plug	
Pin	**Signal Name**	**Pin**	**Signal Name**
6	DSR	20	DTR
7	RTS	no connection	—
8	CTS	20	DTR

To print, the communication parameters (baud rate, data bits and parity) of the instrument and the printer must match.

6.2.2 Connecting to a Personal Computer

Connect the colorimeter to a personal computer (PC) with the computer interface cable (Cat. No. 48129-00) listed under *REPLACEMENT PARTS* on page *69*. The cable provides a direct link between the colorimeter and the 9-pin D connector used for the serial port on most personal computers. If your computer has a 25-pin D connector, use a 9-pin to 25-pin adapter (available at most computer supply stores).

Use a communications software, such as HachLink™ Software (Cat. No. 49665-00) to collect data from the instrument. HachLink is a Windows-based application that allows a personal computer to capture data from several Hach instruments, including the DR/800 Series Colorimeters.

The captured data can be stored in a text file as a spread-sheet compatible format or as free-format text. Data captured in the spreadsheet format is easily transferred into most spreadsheet programs (i.e., Excel®, Microsoft Works®, Lotus 123®) for graphing and reporting.

To install and run HachLink™ Software, the computer and software must meet the following minimum requirements:

- IBM PC/AT or compatible with a 386SX processor (16 MHz or better)
- 4 megabytes of RAM
- Hard disk drive with 2 megabytes or more of free space

- 3-1/2 inch, 1.44 megabyte floppy disk drive
- VGA graphics with 640 x 480 or higher resolution, 16 or more colors
- Mouse or other pointing device
- A 9-pin serial port (or 25-pin serial port with 9-pin adapter)
- Windows 3.1 or later
- DOS 3.3 or later

To transfer data, the communication parameters (baud rate, data bits and parity) of the instrument and the computer must match. Once the communication link is established, press **PRINT** to send data to the computer.

6.3 Sending Data to a Printer or Computer

A permanent record of test results may be obtained using the DTA RS232 serial output to drive a printer or by transferring the data to a computer for storage. Data displayed on the instrument screen may be sent to an accessory printer or computer by attaching the DTA to the instrument and pressing the **PRINT** key. The data can be data recalled from memory or the current sample reading. Only the information shown on the display will be printed.

6.3.1 Sending Currently Displayed Data

To transfer currently displayed data:

1. Remove the instrument cap and slide the DTA onto the instrument until snug.
2. Make sure the DTA is properly connected to the computer or printer. See *Section 6.2 RS232 Connections.*
3. Press the **PRINT** key. Four dashes and **PRINT** are displayed while the data is being transmitted to the DTA.

6.3.2 Sending Recalled Data

To transfer recalled data:

1. Remove the instrument cap and slide the DTA onto the instrument until snug.
2. Make sure the DTA is properly connected to the computer or printer. (See *Section 6.2 RS232 Connections*.)
3. Recall the data to be transferred (see *Section 5.1 Recalling Data* on page *43*).
4. When sample data is displayed, press the **PRINT** key. Four horizontal lines and **PRINT** are displayed while the data is transmitted to the DTA.

6.3.3 Sending All Stored Data

All data stored in memory may be sent to a printer or computer via the **SETUP** menu option as follows:

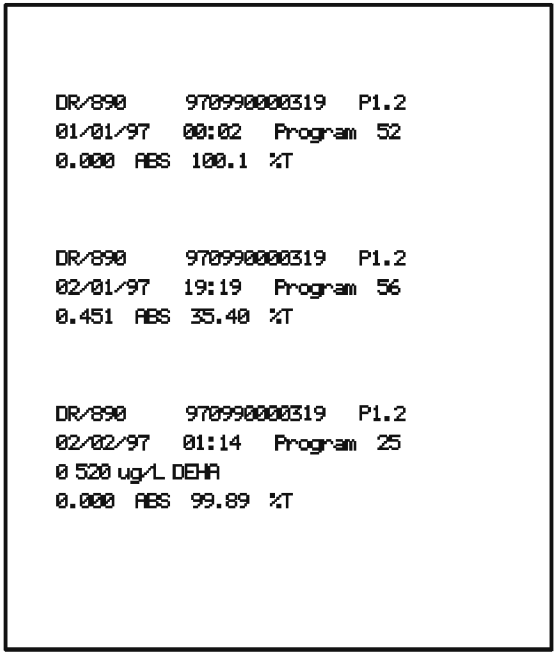
1. Remove the instrument cap and slide the DTA onto the instrument until snug.
2. Make sure the DTA is properly connected to the computer or printer. (See *Section 6.2 RS232 Connections*.)
3. Press the **SETUP** key.
4. Scroll, using the down **ARROW** key, to the **PRINT** option.
5. Press the **ENTER** key when the word **ALL** is displayed above **PRINT**. All stored data is now sent to the DTA. After the data has been successfully sent, the instrument defaults to the last used program.

Transferred data will include the following information:

- instrument model number
- instrument serial number
- instrument software version
- date

- time
- program number
- sample number
- concentration
- units
- chemical form
- Overrange errors (limit)
- absorbance
- %T

Figure 11 Printed Data Format



SECTION 7 MAINTENANCE

7.1 Cleaning the Colorimeter

Use a damp cloth to wipe the outside of the colorimeter enclosure. Wipe up spills promptly. Use cotton swabs to clean and dry the sample compartment if any spillage occurs.

Keep the colorimeter and sample cells clean at all times. Use a lens tissue or a soft, lint-free cloth (that will not leave an oil film) to wipe out the sample cell.

7.1.1 Cleaning the Data Transfer Adapter

Little cleaning is required of this adapter. Clean the outside and inside with a barely damp cloth. Wipe up spills promptly.

7.1.2 Sample Cells

Clean sample cells with detergent, rinse several times with tap water, and then rinse thoroughly with deionized water. Some cells may require acid washing or other special cleaning procedures. Refer to the Procedures Manual for additional information. Rinse sample cells used with organic solvents (chloroform, benzene, toluene, etc.) with acetone before the detergent wash, and again as a final rinse before drying.

7.2 Replacement Instructions

To prevent static electricity damage to the instrument, always turn the instrument off before removing the batteries.

7.2.1 Battery Replacement

When the **LOW BATTERY** icon appears in the display the batteries must be replaced or recharged as soon as possible to ensure proper instrument performance. Turn the instrument off before removing the battery compartment door.

The correct date and time may need to be reentered after battery replacement. See *Section 2.3 Setting the Date and Time*.

See *Section 2.1 Battery Installation* for complete installation instructions.

SECTION 8 TROUBLESHOOTING

8.1 Introduction

Correcting problem conditions with the DR/800 Series Colorimeters in the field is limited to responding to the error messages presented in the display. Other problems must be handled by a Hach technician at a service center. Refer to *REPAIR SERVICE*. **Do not** attempt to service anything other than the battery; there are no other field-serviceable parts. Opening the instrument case will void the warranty.

8.1.1 Error Codes

This feature identifies the problem area or areas when an error indication occurs during instrument operation. When an error occurs, **ERROR** displays on the screen, followed by a number which refers to a diagnostic error code. Refer to *Table 6* below to determine the error cause and possible corrective actions. Turn the instrument off, then on, to restore the instrument to operation.

Table 6 Error Codes

ERROR Code Number	Error Code Type	Corrective Action
1	Unconfigured instrument	Contact Hach Instrument Service Department
2	Could not read program data	Contact Hach Instrument Service Department
3	Could not write program data	Contact Hach Instrument Service Department
4	Measurement battery error	Replace instrument batteries
5	Measurement A/D error	Contact Hach Instrument Service Department
6	Measurement offset error	Check to be sure instrument light shield (cap) is correctly installed
7	Measurement low light error	Check for light path blockage Zero is out of instrument range; dilute to within range Contact Hach Instrument Service Department
8	Measurement over-range error	Make sure instrument cap is properly installed Contact Hach Instrument Service Department

8.1.2 Beeper/Error Icon

When a key is pressed that calls for the instrument to perform a function that is not available at that time, the beeper is activated once and the error icon appears on the display. Each time the unacceptable command is entered, one beep sounds.

If an unavailable program number is entered, the beeper also sounds. Program numbers must range from 101 to 105 (user programs) and 1 to 100 (Hach programs). Entering a number other than these results in the beeper sound and the error icon briefly illuminates. After this beep sounds, re-enter the proper number.

8.1.3 Concentration Out of Range

An out-of-range condition is indicated by the illuminated **LIMIT** icon. It means the sample concentration exceeds the range of the programmed calibration. Make sure the test procedure is followed correctly, dilute the sample (for over range samples) and rerun the test. Each Hach test has an upper concentration value that defines the program range. Measurements beyond that range are unreliable.

8.1.4 Low Battery

The instrument continuously monitors battery voltage. If the battery voltage falls to a level which indicates less than ten percent battery life remains, the instrument automatically warns the operator by displaying the **LOW BATTERY** icon. Replace the batteries as soon as possible for most reliable instrument performance.

APPENDIX A AVAILABLE PARAMETERS AND RANGES

Table 7 DR/820 Chemistries

PARAMETER	Primary Form	Alternate Forms	Test Range of Primary Form (mg/L or as noted)	Program number
Aluminum, Aluminon	Al	Al_2O_3	0 - 0.800	1
Bromine	Br_2	—	0 - 4.50	5
Bromine, AV	Br_2	—	0 - 4.50	6
Chlorine, free, HR	Cl_2	—	0 - 5.00	8
Chlorine, total, HR	Cl_2	—	0 - 5.00	8
Chlorine, free	Cl_2	—	0 - 2.00	9
Chlorine, total	Cl_2	—	0 - 2.00	9
Chlorine, free, AV	Cl_2	—	0 - 2.00	11
Chlorine, total, AV	Cl_2	—	0 - 2.00	11
Chlorine, free, Test 'N Tube	Cl_2	—	0 - 5.00	10
Chlorine, total, Test 'N Tube	Cl_2	—	0 - 5.00	10
Chlorine Dioxide	ClO_2	—	0 - 5.00	112
Chlorine Dioxide, AV	ClO_2	—	0 - 5.00	113
COD, Manganese III	COD	—	20 - 1000	18
Cyanuric acid	CYACD	—	0 - 55	24
Hardness, calcium	$CaCO_3$	Ca	0 - 4.00	29
Hardness, magnesium	$CaCO_3$	Mg, $MgCO_3$	0 - 4.00	30
Iron, Ferrous	Fe	—	0 - 3.00	33
Iron, Ferrous, AV	Fe	—	0 - 3.00	33
Iron, total, FerroVer	Fe	—	0 - 3.00	33
Iron, total, FerroVer, AV	Fe	—	0 - 3.00	33
Manganese, HR	Mn	MnO_4, $KMnO_4$	0 - 20.0	41
Nitrate, HR, AV	NO_3-N	NO_3	0 - 30.0	50
Nitrate, HR	NO_3-N	NO_3	0 - 30.0	51
Nitrate, LR	NO_3-N	NO_3	0 - 0.50	55
Nitrite, LR	NO_2-N	NO_2, $NaNO_2$	0 - 0.350	60
Nitrite, LR, AV	NO_2-N	NO_2, $NaNO_2$	0 - 0.350	62
Nitrite, TNT	NO_2-N	NO_2, $NaNO_2$	0 - 0.500	63
Oxygen, dissolved, HR, AV	O_2	—	0 - 15.0	70
pH	pH	—	6.5 - 8.5 pH	75
Phosphorous, amino acid	PO_4	P, P_2O_5	0 - 30.0	85
Sulfate	SO_4	—	0 - 70	91
Sulfate, AV	SO_4	—	0 - 70	92
Turbidity	FAU	—	0 - 1000 FAU	95
Volatile Acids	HOAc	—	0 - 2800	96

Table 8 DR/850 Chemistries

PARAMETER	Primary Form	Alternate Forms	Test Range of Primary Form (mg/L or as noted)	Program number
Aluminum, Aluminon	Al	Al_20_3	0 - 0.800	1
Bromine	Br_2	—	0 - 4.50	5
Bromine, AV	Br_2	—	0 - 4.50	6
Chlorine, free, HR	Cl_2	—	0 - 5.00	8
Chlorine, total, HR	Cl_2	—	0 - 5.00	8
Chlorine, free	Cl_2	—	0 - 2.00	9
Chlorine, total	Cl_2	—	0 - 2.00	9
Chlorine, free, AV	Cl_2	—	0 - 2.00	11
Chlorine, total, AV	Cl_2	—	0 - 2.00	11
Chlorine, free, Test 'N Tube	Cl_2	—	0 - 5.00	10
Chlorine, total, Test 'N Tube	Cl_2	—	0 - 5.00	10
Chlorine Dioxide	ClO_2	—	0 - 5.00	112
Chlorine Dioxide, AV	ClO_2	—	0 - 5.00	113
COD, HR, HR+	COD	—	0 - 1500, 0-15,000	17
COD, Manganese III	COD	—	20 - 1000	18
Cyanide	CN	—	0 - 0.240	23
Cyanuric acid	CYACD	—	0 - 55	24
Detergents	LAS	—	0 - 0.30	26
Fluoride, SPADNS	F	—	0 - 2.00	27
Fluoride, SPADNS, AV	F	—	0 - 2.0	28
Hardness, calcium	$CaCO_3$	Ca	0 - 4.00	29
Hardness, magnesium	$CaCO_3$	Mg, $MgCO_3$	0 - 4.00	30
Iron, Ferrous	Fe	—	0 - 3.00	33
Iron, Ferrous, AV	Fe	—	0 - 3.00	33
Iron, total, FerroVer	Fe	—	0 - 3.00	33
Iron, total, FerroVer, AV	Fe	—	0 - 3.00	33
Iron, total, FerroMo	Fe	—	0 - 1.80	38
Iron, total, TPTZ	Fe	—	0 - 1.80	39
Iron, total, TPTZ, AV	Fe	—	0 - 1.80	39
Manganese, HR	Mn	MnO_4, $KMnO_4$	0 - 20.0	41
Molybdenum, ternary complex	Mo^6	MoO_4	0 - 3.00	47
Nitrogen, monochloramine and free ammonia, Salicylate	N	Cl_2, NH_3	0 - 0.50	49

Table 8 DR/850 Chemistries (Continued)

PARAMETER	Primary Form	Alternate Forms	Test Range of Primary Form (mg/L or as noted)	Program number
Nitrogen, monochloramine and free ammonia, Salicylate, AV	N	Cl_2, NH_3	0 - 0.50	49
Nitrate, HR, AV	NO_3-N	NO_3	0 - 30.0	50
Nitrate, HR	NO_3-N	NO_3	0 - 30.0	51
Nitrate, LR	NO_3-N	NO_3	0 - 0.50	55
Nitrite, LR	NO_2-N	NO_2, $NaNO_2$	0 - 0.350	60
Nitrite, LR, AV	NO_2-N	NO_2, $NaNO_2$	0 - 0.350	62
Nitrite, TNT	NO_2-N	NO_2, $NaNO_2$	0 - 0.500	63
Nitrogen, Ammonia, Salicylate	NH_3-N	NH_3 , NH_4	0 - 0.50	64
Nitrogen, Ammonia, LR, TNT	NH_3-N	NH_3	0 - 2.50	66
Nitrogen, Ammonia, HR, TNT	NH_3-N	NH_3	0 - 50	67
Nitrogen, Total Inorganic, TNT	N	NH_3	0 - 25.0	68
Oxygen, dissolved, HR, AV	O_2	—	0 - 15.0	70
Oxygen, dissolved, LR, AV	O_2	—	0 - 1000 µg/L	71
Ozone, LR, AV	O_3	—	0 - 0. 25	72
Ozone, MR, AV	O_3	—	0 - 1.50	73
Ozone, HR, AV	O_3	—	0 - 0.75	74
pH	pH	—	6.5 - 8.5 pH	75
Phosphonates	PO_4	—	0-125	80
Phosphorous, PhosVer 3	PO_4	P, P_2O_5	0 - 2.50	79
Phosphorous, PhosVer 3, AV	PO_4	P, P_2O_5	0 - 2.50	79
Phosphorous, total, PhosVer 3	PO_4	P, P_2O_5	0 - 2.5	79
Phosphorous, acid hydrolyzable, PhosVer 3	PO_4	P, P_2O_5	0 - 2.5	79
Phosphorous, PhosVer 3, TNT	PO_4	P, P_2O_5	0 - 5.0	82
Phosphorous, total, PhosVer 3, TNT	PO_4	P, P_2O_5	0 - 3.50	82
Phosphorous, acid hydrolyzable, PhosVer 3, TNT	PO_4	P, P_2O_5	0 - 5.00	82
Phosphorous, amino acid	PO4	P, P_2O_5	0 - 30	85
Silica, LR	SiO2	—	0 - 1.60	90
Sulfate	SO_4	—	0 - 70	91
Sulfate, AV	SO_4	—	0 - 70	92
Sulfide	S	—	0 - 0.70	93

Table 8 DR/850 Chemistries (Continued)

PARAMETER	Primary Form	Alternate Forms	Test Range of Primary Form (mg/L or as noted)	Program number
Suspended Solids	SuSld	—	0 - 750	94
Tannin and Lignin	tanic	—	0 - 9.0	98
Toxicity	Toxic	—	0 - 100% Inhibition	61
Turbidity	FAU	—	0 - 1000 FAU	95
Volatile Acids	HOAc	—	0 - 2800	96
Zinc	Zn	—	0 - 3.00	97

Table 9 DR/890 Chemistries

PARAMETER	Primary Form	Alternate Forms	Test Range of Primary Form (mg/L or as noted)	Program number
Aluminum, Aluminon	Al	Al_20_3	0 - 0.800	1
Boron	B	H_3BO_3	0 - 1.60	4
Bromine	Br_2	—	0 - 4.50	5
Bromine, AV	Br_2	—	0 - 4.50	6
Chlorine Dioxide, MR	ClO_2	—	0 - 50	7
Chlorine, free, HR	Cl_2	—	0 - 5.00	8
Chlorine, total, HR	Cl_2	—	0 - 5.00	8
Chlorine, free	Cl_2	—	0 - 2.00	9
Chlorine, total	Cl_2	—	0 - 2.00	9
Chlorine, free, AV	Cl_2	—	0 - 2.00	11
Chlorine, total, AV	Cl_2	—	0 - 2.00	11
Chlorine, free, Test ‘N Tube	Cl_2	—	0 - 5.00	10
Chlorine, total, Test ‘N Tube	Cl_2	—	0 - 5.00	10
Chlorine Dioxide	ClO_2	—	0 - 5.00	112
Chlorine Dioxide, AV	ClO_2	—	0 - 5.00	113
Chromium, Hexavalent	Cr^6	CrO_4, Cr_2O_7	0 - 0.60	13
Chromium, Hexavalent, AV	Cr^6	CrO_4, Cr_2O_7	0 - 0.60	14
Chromium, total	Cr	—	0 - 0.60	15
COD, LR	COD	—	0 - 150	16
COD, HR, HR+	COD	—	0 - 1500, 0 - 15000	17
COD, Manganese III	COD	—	20 - 1000	18
Color	Pt Co	—	0 - 500 APHA color	19
Copper, Bichinchoninate	Cu	—	0 - 5.00	20

Table 9 DR/890 Chemistries (Continued)

PARAMETER	Primary Form	Alternate Forms	Test Range of Primary Form (mg/L or as noted)	Program number
Copper, Bichinchoninate, AV	Cu	—	0 - 5.00	21
Copper, porphyrin	Cu	—	0 - 210.0 µg/L	22
Cyanide	CN	—	0 - 0.240	23
Cyanuric acid	CYACD	—	0 - 55	24
DEHA	DEHA	—	0 - 500 µg/L	25
Detergents	LAS	—	0 - 0.30	26
Fluoride, SPADNS	F	—	0 - 2.00	27
Fluoride, SPADNS, AV	F	—	0 - 2.00	28
Hardness, calcium	$CaCO_3$	Ca	0 - 4.00	29
Hardness, magnesium	$CaCO_3$	Mg, $MgCO_3$	0 - 4.00	30
Hydrazine	N_2H_4	—	0 - 500 µg/L	31
Hydrazine, AV	N_SH_4	—	0 - 500 µg/L	32
Immunoassay, PCB	—	—	threshold	42
Immunoassay, TPH	—	—	threshold	42
Immunoassay, TPH in water	—	—	threshold	42
Iron, Ferrous	Fe	—	0 - 3.00	33
Iron, Ferrous, AV	Fe	—	0 - 3.00	33
Iron, total, FerroVer	Fe	—	0 - 3.00	33
Iron, total, FerroVer, AV	Fe	—	0 - 3.00	33
Iron, total, Ferrozine	Fe	—	0 - 1.300	37
Iron, total, FerroMo	Fe	—	0 - 1.80	38
Iron, total, TPTZ	Fe	—	0 - 1.80	39
Iron, total, TPTZ, AV	Fe	—	0 - 1.80	39
Manganese, HR	Mn	MnO_4, $KMnO_4$	0 - 20.0	41
Manganese, LR	Mn	MnO_4, $KMnO_4$	0 - 0.700	43
Molybdenum, Molybdate, HR	Mo^6	MoO_4	0 - 40.0	44
Molybdenum, Molybdate, HR, AV	Mo^6	MoO_4	0 - 40.0	44
Molybdenum, ternary complex	Mo^6	MoO_4	0 - 3.00	47
Nickel, PAN	Ni	—	0 - 1.000	48
Nitrogen, monochloramine and free ammonia, Salicylate	N	Cl_2, NH_3	0 - 0.50	49
Nitrogen, monochloramine and free ammonia, Salicylate, AV	N	Cl_2, NH_3	0 - 0.50	49
Nitrate, HR, AV	NO_3-N	NO_3	0 - 30.0	50

Table 9 DR/890 Chemistries (Continued)

PARAMETER	Primary Form	Alternate Forms	Test Range of Primary Form (mg/L or as noted)	Program number
Nitrate, HR	NO_3-N	NO_3	0 - 30.0	51
Nitrate, Cd reduction, MR, AV	NO_3-N	NO_3	0 - 5.0	53
Nitrate, Cd reduction, MR	NO_3-N	NO_3	0 - 5.0	54
Nitrate, LR	NO_3-N	NO_3	0 - 0.50	55
Nitrate, TNT, chromotropic acid finish	NO_3-N	NO_3	0 - 30.0	57
Nitrogen, TN, TNT, chromotropic acid	N	NO_3, NH_3	0 - 25	58
Nitrite, HR	NO_2	NO_2-N, $NaNO_2$	0 - 150	59
Nitrite, LR	NO_2-N	NO_2, $NaNO_2$	0 - 0.350	60
Nitrite, LR, AV	NO_2-N	NO_2, $NaNO_2$	0 - 0.350	62
Nitrite, TNT	NO_2-N	NO_2, $NaNO_2$	0 - 0.500	63
Nitrogen, Ammonia, Salicylate	NH_3-N	NH_3 , NH_4	0 - 0.50	64
Nitrogen, TKN with Nessler finish	TKN	—	0 - 150	65
Nitrogen, Ammonia, LR, TNT	NH_3-N	NH_3	0 - 2.50	66
Nitrogen, Ammonia, HR, TNT	NH_3-N	NH_3	0 - 50	67
Nitrogen, Total Inorganic TNT	N	NH_3	0 - 25.0	68
Nitrogen, Total, HR, TNT	N	NH_3	10 - 150	69
Oxygen, dissolved, HR, AV	O_2	—	0 - 15.0	70
Oxygen, dissolved, LR, AV	O_2	—	0 - 1000 µg/L	71
Ozone, LR, AV	O_3	—	0 - 0.25	72
Ozone, MR, AV	O_3	—	0 - 0.75	73
Ozone, HR, AV	O_3	—	0 - 1.50	74
pH	pH	—	6.5 - 8.5 pH	75
Phosphonates	PO_4	—	0 - 125	80
Phosphorous, Molybdovanadate	PO_4	P, P_2O_5	0 - 45.0	77
Phosphorous, Molybdovanadate, AV	PO_4	P, P_2O_5	0 - 45.0	78
Phosphorous, PhosVer 3	PO_4	P, P_2O_5	0 - 2.50	79
Phosphorous, PhosVer 3, AV	PO_4	P, P_2O_5	0 - 2.50	79
Phosphorous, total, PhosVer 3	PO_4	P, P_2O_5	0 - 2.5	79
Phosphorous, acid hydrolyzable, PhosVer 3	PO_4	P, P_2O_5	0 - 2.5	79
Phosphorous, PhosVer 3, TNT	PO_4	P, P_2O_5	0 - 5.0	82

Table 9 DR/890 Chemistries (Continued)

PARAMETER	Primary Form	Alternate Forms	Test Range of Primary Form (mg/L or as noted)	Program number
Phosphorous, total, PhosVer 3, TNT	PO_4	P, P_2O_5	0 - 3.50	82
Phosphorous, acid hydrolyzable, PhosVer 3, TNT	PO_4	P, P_2O_5	0 - 5.00	82
Phosphorous, amino acid	PO_4	P, P_2O_5	0 - 30.0	85
Phosphorus, Reactive, HR, TNT	PO_4^{3-}	P, P_2O_5	0 - 100.0	86
Phosphorus, Total, HR, TNT	PO_4^{3-}	P, P_2O_5	0 - 100.0	87
Silica, UHR	SiO_2	—	0 - 200	88
Silica, HR	SiO_2	—	0 - 75.0	89
Silica, LR	SiO_2	—	0 - 1.60	90
Sulfate	SO_4	—	0 - 70	91
Sulfate, AV	SO_4	—	0 - 70	92
Sulfide	S	—	0 - 0.70	93
Suspended Solids	SuSld	—	0 - 750	94
Triazole, Benzotriazole	BENZO	TOLY	0 - 16.0	3
Triazole, Tolytriazole	TOLY	BENZO	0 - 16.0	3
Tannin and Lignin	Tanic	—	0 - 9.0	98
Toxicity	Toxic	—	0 - 100% Inhibition	61
Turbidity	FAU	—	0 - 1000 FAU	95
Volatile Acids	HOAc	—	0 - 2800	96
Zinc	Zn	—	0 - 3.00	97

GENERAL INFORMATION

At Hach Company, customer service is an important part of every product we make.

With that in mind, we have compiled the following information for your convenience.

REQUIRED APPARATUS

Description	Unit	Cat. No.
Adapter, Assembly, COD	each	48464-00
Batteries, Alkaline AA	pkg/4	19380-04
Battery Cover Assembly	each	48455-00
Battery Holder for 4 Alkaline AA cells	each	48434-00
Manual Set, DR/890, includes Instrument & Procedure Manual & Binder	each	48470-77
Manual Set, DR/850, includes Instrument & Procedure Manual & Binder	each	48450-77
Manual Set, DR/820, includes Instrument & Procedure Manual & Binder	each	48440-77
Sample Cell, 25 x 95 mm 10-20-25 mL	pkg/6	24019-06

OPTIONAL ACCESSORIES

Adapter, Immunoassay	each	48467-00
Adapter, Data Transfer, RS232, includes 48129-00 cable	each	48490-00
Batteries, Rechargeable, NiCad, for PN60 Printer	each	26688-00
Batteries, Rechargeable, Alkaline AA, for DR/800 Series Colorimeter	pkg/4	49427-00
Battery Charger, Alkaline AA 115 VAC UL Approved	each	49428-00
Cap, Sample Cell, for 25 x 95 mL cell	pkg/12	24018-12
Carrying Case, DR/800 Series Colorimeter, hard-sided	each	49425-00
Carrying Case, DR/800 Series Colorimeter, soft-sided w/shoulder strap	each	27220-00
Carrying Case, Portable Laboratory	each	49430-00
Computer Interface Cable, 6 ft., for use with the DTA	each	48129-00
DR/Check™ ABS Standards	set	27639-00
Foot, Rubber, DR/800 Series Colorimeter	each	49424-00
HachLink Software	each	49665-00
Instrument Cap	each	49431-00
Power Cord for PN60 Printer, European Plug	each	46836-00
Printer, 115/230V, Citizen PN60*	each	26687-00
Printer Cable Assembly	each	26689-00
Printer Ink Cartridge, for PN60 Printer, Black	pkg/2	26690-00

* Requires Data Transfer Adapter

HOW TO ORDER

How To Order Within The United States

By phone (in U.S.A.):
6:30 a.m. to 5 p.m. MST
Monday through Friday
800-227-Hach (800-227-4224)
970-669-3050 (Hach Loveland)
By Telex: 160840 (Hach Loveland)

By mail:
Hach Company
P.O. Box 389
Loveland, Colorado 80539-0389
U.S.A.
By FAX: 970-669-2932
(Hach Loveland)

How To Order Outside The United States

Hach maintains a worldwide network of dealers and distributors. Contact your local distributor for help.

In Europe, Mediterranean Africa, and the Middle East:

Hach Europe, S.A./N.V.
Chaussée de Namur, 1
B-5150 Floriffoux (Namur), Belgium
Telephone: (32)(81)44.71.71
FAX: (32)(81)44.13.00

In other areas, obtain assistance from a local Hach distributor or:

Hach Company World Headquarters
P.O. Box 389
Loveland, Colorado 80539-0389
U.S.A.
Telephone: (970) 669-3050
FAX: (970) 669-2932

Hach Sales & Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba R3H 0X4
Telephone: (204) 632-5598
FAX: (204) 694-5134

Information Required

- Hach Account number
- Billing Address
- Your Name and phone number
- Purchase order number
- Catalog number
- Brief description or model number
- Quantity

REPAIR SERVICE

Authorization must be obtained from Hach Company before sending any item for repair. Please contact the Hach Factory Service Center serving your location.

In the United States:

HACH COMPANY
100 Dayton Ave.
P.O. Box 907
Ames, Iowa 50010
800-227-4224 (U.S.A. only)
FAX: (515) 232-1276

In Latin America, the Caribbean, the Far East, the Indian subcontinent, Africa (excluding Mediterranean Africa) or the Pacific Basin:

HACH COMPANY, WORLD HEADQUARTERS
P.O. Box 389
Loveland, Colorado 80539-0389
U.S.A.
Telephone (970) 669-3050
Telex 160840
FAX (970) 669-2932

In Canada:

HACH SALES & SERVICE CANADA LTD.
1313 Border Street, Unit 34
Winnipeg, Manitoba
R3H 0X4
800-665-7635 (Canada only)
(204) 632-5598
FAX: (204) 694-5134

In Europe, the Middle East, or Mediterranean Africa:

HACH EUROPE, S.A./N.V.
Chaussée de Namur, 1
B-51150 Floriffoux (Namur), Belgium
Tel. 32-(0)81-44.71.71

WARRANTY

Hach warrants the DR/800 Series Colorimeters against defective materials or workmanship for one year from the date of shipment.

HACH WARRANTS TO THE ORIGINAL BUYER THAT HACH PRODUCTS WILL CONFORM TO ANY EXPRESS WRITTEN WARRANTY GIVEN BY HACH TO THE BUYER. EXCEPT AS EXPRESSLY SET FORTH IN THE PRECEDING SENTENCE, HACH MAKES NO WARRANTY OF ANY KIND WHATSOEVER WITH RESPECT TO ANY PRODUCTS.
HACH EXPRESSLY DISCLAIMS ANY WARRANTIES IMPLIED BY LAW, INCLUDING BUT NOT LIMITED TO ANY WARRANTY OF MERCHANT-ABILITY OR FITNESS FOR A PARTICULAR PURPOSE.

LIMITATION OF REMEDIES: Hach shall, at its option, replace or repair nonconforming products or refund all amounts paid by the buyer. **THIS IS THE EXCLUSIVE REMEDY FOR ANY BREACH OF WARRANTY.**

LIMITATION OF DAMAGES: IN NO EVENT SHALL HACH BE LIABLE FOR ANY INCIDENTAL OR CONSEQUENTIAL DAMAGES OF ANY KIND FOR BREACH OF ANY WARRANTY, NEGLIGENCE, ON THE BASIS OF STRICT LIABILITY, OR OTHERWISE.

Catalog descriptions, pictures and specifications, although accurate to the best of our knowledge, are not a guarantee or warranty.

For a complete description of Hach Company’s warranty policy, request a copy of our Terms and Conditions of Sale for U.S. Sales from our Customer Service Department.

CERTIFICATION

Hach Company certifies this instrument was tested thoroughly, inspected and found to meet its published specifications when it was shipped from the factory.

The DR/800 Series Colorimeter has been tested and is certified as indicated to the following instrumentation standards:

EN 60825-1: LEDs used in this product are Class 1

Immunity:

EN 50082-1 "1997"(Generic Immunity Standard) per **89/336/EEC EMC**: Supporting test records by Hach Company, certified compliance by Hach Company.

Required Standard/s include:
EN 61000-4-2 (IEC 1000-4-2) Electro-Static Discharge

EN 61000-4-3 (IEC 1000-4-3) Radiated RF Electro-Magnetic Fields

ENV 50204 Radiated Electro-Magnetic Field from Digital Telephones

Emissions:

Per **89/336/EEC EMC**: Supporting test records by Intellistor O.A.T.S., (NVLAP #0369) certified compliance by Hach Company.

Required European Standard/s include:
EN 55011 (CISPR 11) Emissions, Class B Limits

Additional Emissions Standard/s include:

CANADIAN INTERFERENCE-CAUSING EQUIPMENT REGULATION, IECS-003, Class A:
Supporting test records by Intellistor O.A.T.S., certified compliance by Hach Company.

This Class A digital apparatus meets all requirements of the Canadian Interference-Causing Equipment Regulations.

Cet appareil numérique de la classe A respecte toutes les exigences du Règlement sur le matériel brouilleur du Canada.

FCC PART 15, Class "A" Limits:

Supporting test records by Intellistor O.A.T.S., certified compliance by Hach Company.

This device complies with Part 15 of the FCC Rules. Operation is subject to the following two conditions:

(1) This device may not cause harmful interference, and (2) this device must accept any interference received, including interference that may cause undesired operation.

Changes or modifications to this unit not expressly approved by the party responsible for compliance could void the user's authority to operate the equipment.

This equipment has been tested and found to comply with the limits for a Class A digital device, pursuant to Part 15 of the FCC Rules. These limits are designed to provide reasonable protection against harmful interference when the equipment is operated in a commercial environment. This equipment generates, uses, and can radiate radio frequency energy and, if not installed and used in accordance with the instruction manual, may cause harmful interference to radio communications. Operation of this equipment in a residential area is likely to cause harmful interference, in which case the user will be required to correct the interference at his own expense. The following techniques of reducing the interference problems are applied easily.

1. Remove power from the Colorimeter by removing one of its batteries to verify that it is or is not the source of the interference.
2. Move the Colorimeter away from the device receiving the interference.
3. Reposition the receiving antenna for the device receiving the interference.
4. Try combinations of the above.

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FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. - **Call toll-free 800-227-4224**
Outside the U.S.A. - **Contact the HACH office or distributor serving you.**
On the Worldwide Web - **http://www.hach.com**; E-mail - **techhelp@hach.com**

SULFIDE

✔ **Method 8131**

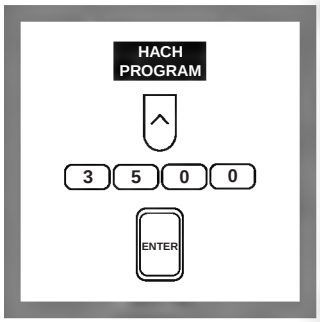
Methylene Blue Method*

(0 to 800 µg/L)

Scope and Application: *For testing total sulfides, H_2S, HS^- and certain metal sulfides in groundwater, wastewater brines and seawater; USEPA accepted for reporting wastewater analysis***

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** Procedure is equivalent to USEPA method 376.2 and Standard Method 4500-S^{2-} D for wastewater.



1. Press the soft key under ***HACH PROGRAM.***

Select the stored program number for sulfide (S^{2-}) by pressing **3500** with the numeric keys.

Press: **ENTER**

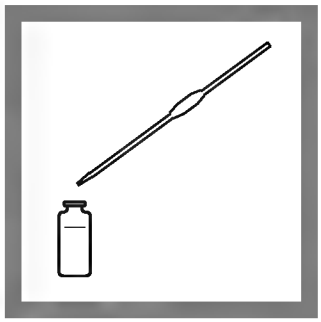
Note: *The Flow Cell and Sipper Modules can be used with this procedure.*

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis. Avoid excessive agitation of samples.*

2. The display will show:

HACH PROGRAM: 3500 Sulfide

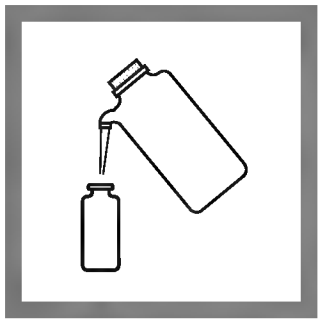
The wavelength (λ), **665 nm**, is automatically selected.



3. Measure 25 mL of sample into a sample cell. This will be the prepared sample.

Note: *For turbid samples, see Interferences (following these steps) for pretreatment instructions.*

Note: *Excessive agitation will cause loss of sulfide. Use a pipet to minimize sulfide loss.*



4. Measure 25 mL of deionized water into a second sample cell (the blank).

5. Add 1.0 mL of Sulfide 1 Reagent to each cell. Swirl to mix.

Note: *Use the calibrated 1-mL dropper.*

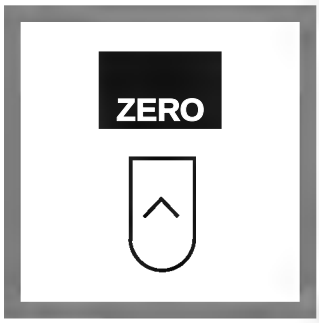
6. Add 1.0 mL of Sulfide 2 Reagent to each cell. Immediately swirl to mix.

Note: *A pink color will develop, then the solution will turn blue if sulfide is present.*

7. Press the soft key under ***START TIMER***.

A 5-minute reaction period will begin.

8. When the timer beeps, place the blank in the cell holder. Close the light shield.



9. Press the soft key under ***ZERO***.

The display will show:

0 µg/L S^{2-}

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

10. Place the prepared sample in the cell holder. Close the light shield. Results in µg/L sulfide (or chosen units) will be displayed.

Note: *Some sulfide loss may occur if dilution is necessary.*

Interferences

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
Strong reducing substances (sulfite, thiosulfate and hydrosulfite)	Interfere by reducing the blue color or preventing its development
Sulfide, high levels	High concentrations of sulfide may inhibit full color development and require sample dilution. Some sulfide loss may occur when the sample is diluted.
Turbidity	For turbid samples, prepare a sulfide-free blank as follows. Use it in place of the deionized water blank in the procedure. **1.** Measure 25 mL of sample into a 50-mL erlenmeyer flask. **2.** Add Bromine Water dropwise with constant swirling until a permanent yellow color just appears. **3.** Add Phenol Solution dropwise until the yellow color just disappears. Use this solution in place of deionized water in step 4.

Sample Collection, Storage and Preservation

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples immediately.

Method Performance

Precision
Standard: 400 µg/L S^{2-}

Program	95% Confidence Limits
3500	399–401 µg/L S^{2-}

For more information on determining precision data and method detection limits, refer to Section *1.5*.

Estimated Detection Limit

Program	EDL
3500	2 µg/L S^{2}

For more information on derivation and use of Hach's estimated detection limit, see Section *1.5.2*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see Section *1.5.1*.

Sensitivity
Program Number: 3500

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	4.9 µg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Determining Soluble Sulfides

Determine soluble sulfides by centrifuging the sample in completely filled, capped tubes and analyzing the supernatant. Insoluble sulfides are then estimated by subtracting the soluble sulfide concentration from the total sulfide result.

Summary of Method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration.

High sulfide levels in oil field waters may be determined after proper dilution.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to *Section 1*.

Pollution Prevention and Waste Management

Sulfide 2 reagent contains potassium dichromate. The final solution will contain hexavalent chromium (D007) at a concentration regulated as a hazardous waste by Federal RCRA. Please see *Section 1* for further information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS

	Cat. No.
Sulfide Reagent Set (100 tests)	22445-00

Includes: (2) 1816-32, (2) 1817-32

Description	Quantity Required per test	Unit	Cat. No.
Sulfide 1 Reagent	2 mL	100 mL MDB	1816-32
Sulfide 2 Reagent	2 mL	100 mL MDB	1817-32
Water, deionized	25 mL	4 liters	272-56

REQUIRED EQUIPMENT AND SUPPLIES

Cylinder, graduated, 25-mL	1	each	508-40
or			
Pipet, volumetric, Class A, 25-mL	1	each	14515-40
DR/4000 1-Inch Cell Adapter	1	each	48190-00
Pipet Filler, safety bulb	1	each	14651-00

OPTIONAL REAGENTS AND STANDARDS

Bromine Water, 30-g/L	29 mL	2211-20
Phenol Solution, 30-g/L	29 mL	2112-20

OPTIONAL EQUIPMENT AND SUPPLIES

DR/4000 Carousel Module Kit	each	48070-02
DR/4000 Flow Cell Module Kit, 1-inch	each	48070-04
DR/4000 Flow Cell Module Kit, 1-cm	each	48070-05
DR/4000 Sipper Module Kit, 1-inch	each	48090-03
Dropper, for 1-oz. bottle	each	2258-00
Flask, Erlenmeyer, 50-mL	each	505-41

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WORLD HEADQUARTERS
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FAX: (970) 669-2932

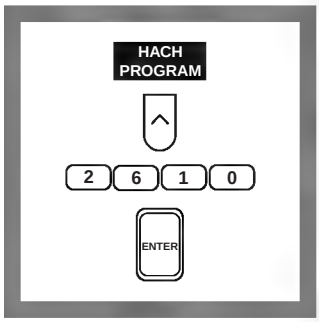
✔ **Method 8507** **Diazotization Method**

Powder Pillows or AccuVac® Ampuls **LR (0 to 0.300 mg/L NO_2^-–N)**

Scope and Application: *For water, wastewater and seawater; USEPA Approved* for wastewater analysis. The estimated detection limit for program numbers 2610 and 2620 are 0.0008 and 0.004 mg/L NO_2^-–N, respectively.*

* *Federal Register, 44(85),* 25505 (May 1, 1979)

Using Powder Pillows



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for low range nitrite by pressing **2610** with the numeric keys.

Press: **ENTER**

Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps.*

Note: *The Flow Cell and Sipper Modules can be used with this procedure. Use 25-mL samples and reagents with the Flow Cell Module.*

2. The display will show:

HACH PROGRAM: 2610 Nitrite, LR

The wavelength (λ), **507 nm**, is automatically selected.

Note: *For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3 through 8, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under* ***ZERO****. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE)****, and then* ***BLANK:OFF****. Enter the reagent blank value and press* **ENTER***. Repeat for each new lot of reagent.*

3. Fill a sample cell with 10 mL of sample.

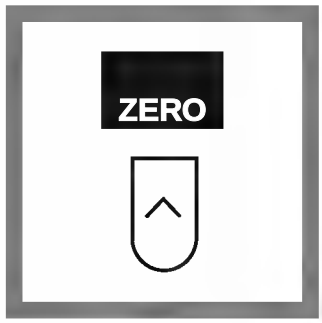
4. Add the contents of one NitraVer 3 Nitrate Reagent Powder Pillow (the prepared sample). Stopper. Shake to dissolve.

Note: *A pink color will develop if nitrite is present.*

5. Press the soft key under ***START TIMER***.

A 20-minute reaction period will begin.

6. When the timer beeps, fill a second sample cell with 10 mL of sample (the blank). Place the blank into the cell holder.



7. Press the soft key under ***ZERO***.

The display will show:

0.0000 mg/L NO_2^-–N

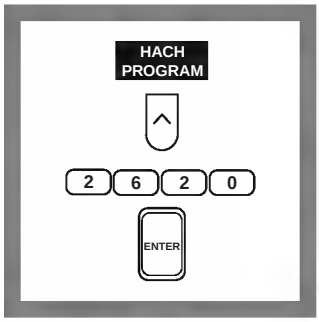
Note: *If you are using a reagent blank correction, the display will show the correction.*

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

8. Remove the stopper. Place the prepared sample into the cell holder. Close the light shield. Result in mg/L nitrite nitrogen (NO_2^-–N) will be displayed.

Note: *The result can be expressed as mg/L nitrite (NO_2^-). Press the soft keys under* ***OPTIONS*** *and then* ***FORM:*** *to scroll through the available options.*

Using AccuVac Ampuls



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for low range nitrite by pressing **2620** with the numeric keys.

Press: **ENTER**

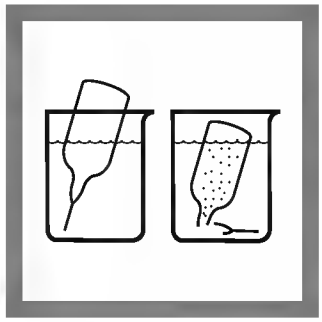
Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps.*

2. The display will show:

HACH PROGRAM: 2620
Nitrate, LR AV

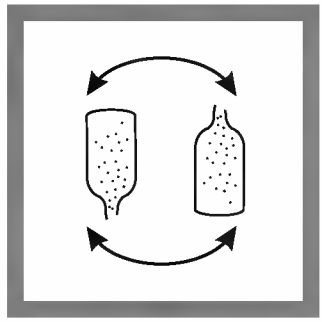
The wavelength (λ), **507 nm**, is automatically selected.

Note: *For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3 through 10, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under* ***ZERO****. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE)****, and then* ***BLANK:OFF****. Enter the reagent blank value and press* **ENTER***. Repeat for each new lot of reagent.*



3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitraVer 3 Nitrate AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills.*

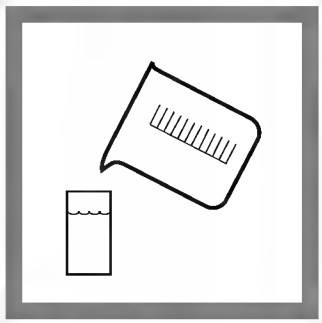


4. Invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A pink color will develop if nitrite is present.*

5. Press the soft key under ***START TIMER***.

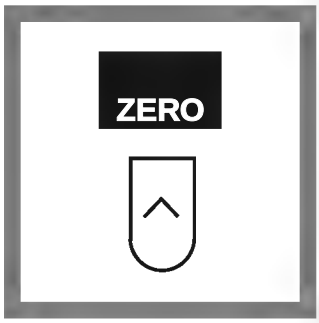
A 20-minute reaction period will begin.



6. When the timer beeps, fill a zeroing vial (the blank) with at least 10 mL of sample.

7. Insert the AccuVac Ampul Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

8. Place the blank into the cell holder. Close the light shield.



9. Press the soft key under ***ZERO***.

The display will show:

0.0000 mg/L NO_2^-–N

Note: *If you are using a reagent blank correction, the display will show the correction.*

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

10. Place the AccuVac Ampul into the cell holder. Close the light shield. Results in mg/L nitrate expressed as nitrogen (NO_2^-–N) will be displayed.

Note: *The results can be expressed as mg/L nitrate (NO_2^-). Press the soft keys under* ***METHOD OPTIONS****, then* ***FORM:*** *to scroll through the available options.*

Interferences

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels
Antiminous ions	Interfere by causing precipitation
Auric ions	Interfere by causing precipitation
Bismuth ions	Interfere by causing precipitation
Chloroplatinate ions	Interfere by causing precipitation
Cupric ions	Cause low results
Ferric ions	Interfere by causing precipitation
Ferrous ions	Cause low results
Lead ions	Interfere by causing precipitation
Mercurous ions	Interfere by causing precipitation
Metavanadate ions	Interfere by causing precipitation
Nitrate	Very high levels of nitrate (>100 mg/L nitrate as N) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels.
Silver ions	Interfere by causing precipitation
Strong oxidizing and reducing substances	Interfere at all levels

Sample Collection, Storage and Preservation

Collect samples in clean plastic or glass bottles. Store at 4 °C (30 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test.

Accuracy Check

Standard Solution Method
Preparing nitrite standards is difficult. A standard should be prepared by a trained chemist. Hach recommends using the standard preparation instructions in *Standard Methods for the Examination of Water and Wastewater,* Method 4500-NO_2^- B (p. 4–86 of 18th edition) Prepare a 0.150-mg/L standard.

Method Performance

Precision

Standard: 0.1500 mg/L NO_2^-–N

Program	95% Confidence Limits
2610	0.1494–0.1506 mg/L NO_2^-–N
2620	0.1496–0.1504 mg/L NO_2^-–N

For more information on determining precision data and method detection limits, refer to Section *1.5*.

Estimated Detection Limit

Program	EDL
2610	0.0008 mg/L NO_2^-–N
2620	0.0043 mg/L NO_2^-–N

For more information on derivation and use of Hach's estimated detection limit, see Section *1.5.2*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see Section *1.5.1*.

Sensitivity
Program Number: 2610

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	0.00187 mg/L

Program Number: 2620

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	0.00203 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

Preparing nitrite standards is difficult. Calibration should be performed by a trained chemist. Hach recommends using the standard preparation instructions in *Standard Methods for the Examination of Water and Wastewater,* Method 4500-NO_2^- B (p. 4–86 of 18th edition).

Using the standards prepared above and the analysis procedure, generate a calibration curve.

Summary Of Method

Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite present.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to Section *1*.

Pollution Prevention and Waste Management

For information on pollution prevention and waste management, refer to Section *1*.

REQUIRED REAGENTS AND STANDARDS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 3 Nitrite Reagent Powder Pillows	1 pillow	100/pkg	21071-69

REQUIRED REAGENTS AND STANDARDS (Using AccuVac Ampuls)

NitriVer 3 Nitrite Reagent AccuVac Ampul	1 ampul	25/pkg	25120-25

REQUIRED EQUIPMENT AND SUPPLIES (Using Powder Pillows)

DR/4000 1-Inch Cell Adapter	1	each	48190-00
Sample Cells, matched pair, 1-inch, glass, with stoppers	2	pair	26126-02

REQUIRED EQUIPMENT AND SUPPLIES (Using AccuVac Ampuls)

Beaker, 50-mL	1	each	500-41
DR/4000 AccuVac Ampul Adapter	1	each	48187-00
Sample Cell, with cap (zeroing vial)	1	each	21228-00

OPTIONAL REAGENTS AND STANDARDS

Sodium Nitrite, ACS	454 g		2452-01
Water, deionized	4 liters		272-56

OPTIONAL EQUIPMENT AND SUPPLIES

Balance, analytical, 110 VAC		each	26103-00
Balance, analytical, 220 VAC		each	26103-02
DR/4000 Carousel Module Kit		each	48070-02
DR/4000 Flow Cell Module Kit, 1-inch		each	48070-04
DR/4000 Flow Cell Module Kit, 1-cm		each	48070-05
DR/4000 Sipper Module Kit, 1-inch		each	48090-03
Flask, volumetric, 1000-mL, Class B		each	547-53
Pipet, serological, 10-mL		each	532-38
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet, volumetric, Class A, 1.00-mL		each	14515-35
Pipet Filler, safety bulb		each	14651-00

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IRON, Ferrous

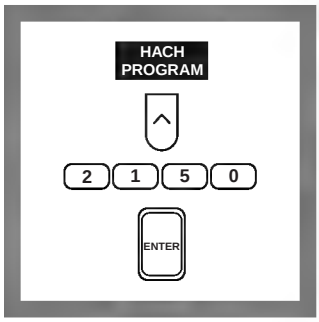
Method 8146 **1,10 Phenanthroline Method***

Powder Pillows or AccuVac® Ampuls **(0 to 3.000 mg/L)**

Scope and Application: *For water, wastewater and seawater. The estimated detection limit for program numbers 2150 and 2155 are 0.008 and 0.007 mg/L Fe^{2+}, respectively.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater,* 15th ed. 201 (1980)

Using Powder Pillows



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for ferrous iron (Fe^{2+}), by pressing **2150** with the numeric keys.

Press: **ENTER**

Note: *Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric iron, which is not determined. See Sample Collection, Storage and Preservation following these steps.*

Note: *The Flow Cell and Sipper Modules can be used with this procedure.*

2. The display will show:

HACH PROGRAM: 2150
Iron, Ferrous

The wavelength (λ), **510 nm**, is automatically selected.

3. Fill a clean sample cell with 25 mL of sample.

Note: *For proof of accuracy, use a 1.0 mg/L ferrous iron standard solution (preparation given in the Accuracy Check section) in place of the sample.*

Note: *For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3 through 10, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under* ***ZERO****. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE)****, and then* ***BLANK:OFF****. Enter the reagent blank value and press* **ENTER***. Repeat for each new lot of reagent.*

4. Add the contents of one Ferrous Iron Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

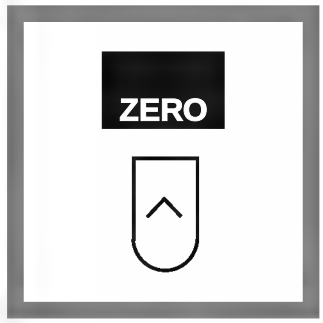
Note: *An orange color will form if ferrous iron is present.*

5. Press the soft key under ***START TIMER***.

A 3-minute reaction period will begin.

6. Fill a second sample cell with 25 mL of sample (the blank).

7. When the timer beeps, place the blank into the cell holder. Close the light shield.



8. Press the soft key under ***ZERO***.

The display will show:

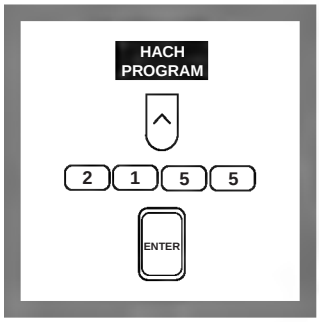
0.000 mg/L Fe^{2+}

Note: *If you are using a reagent blank correction, the display will show the correction.*

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

9. Place the prepared sample into the cell holder. Close the light shield. The results in mg/L Fe^{2+} (or chosen units) will be displayed.

Using AccuVac Ampuls



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for ferrous iron (Fe^{2+}) by pressing **2155** with the numeric keys.

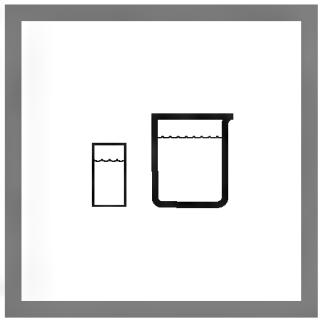
Press: **ENTER**

Note: *Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric iron, which is not determined. See Sample Collection, Storage and Preservation following these steps.*

2. The display will show:

HACH PROGRAM: 2155
Iron, Ferrous AV

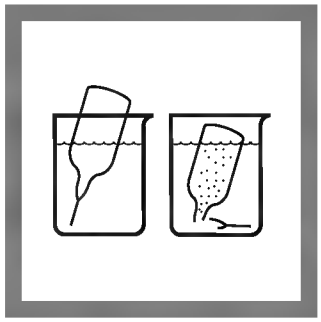
The wavelength (λ), **510 nm**, is automatically selected.



3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

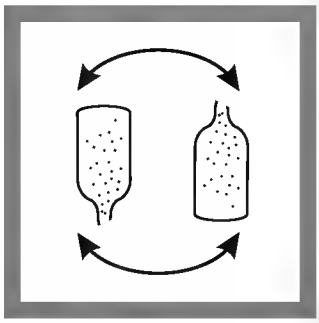
Note: *For proof of accuracy, a 1.0-mg/L ferrous iron standard solution (preparation given in the Accuracy Check section) can be used in place of the sample.*

Note: *For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating Steps 3 through 10, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under* ***ZERO****. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE)****, and then* ***BLANK:OFF****. Enter the reagent blank value and press* **ENTER***. Repeat for each new lot of reagent.*



4. Fill a Ferrous Iron AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *An orange color will form if ferrous iron is present.*

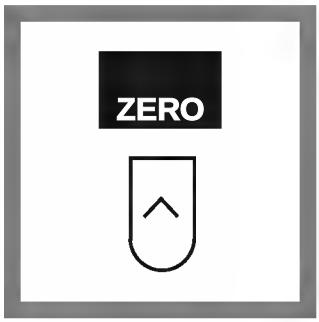
6. Press the soft key under ***START TIMER***.

A 3-minute reaction period will begin.

Note: *Complete Step 7 during the reaction period.*

7. Insert the AccuVac Ampul Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

8. When the timer beeps place the blank into the cell holder. Close the light shield.



9. Press the soft key under ***ZERO***.

The display will show:

0.000 mg/L Fe^{2+}

Note: *If you are using a reagent blank correction, the display will show the correction.*

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

10. Place the AccuVac Ampul into the cell holder. Close the light shield. Results in mg/L Fe^{2+} (or chosen units) will be displayed.

Sample Collection, Storage and Preservation

Collect samples in plastic or glass bottles. Analyze samples as soon as possible after collection.

Accuracy Check

Standard Solution Method

Prepare a ferrous iron stock solution (100-mg/L Fe^{2+}) by dissolving 0.7022 grams of Ferrous Ammonium Sulfate, hexahydrate, in deionized water. Dilute to one liter in a Class A volumetric flask. In a 100-mL Class A volumetric flask, dilute 1.00 mL of this solution to 100 mL with deionized water to make a 1.0-mg/L standard solution. Prepare this solution immediately before use. Perform the iron procedure as described above.

To adjust the calibration curve using the reading obtained with the 1.0 mg/L Fe^{2+} Standard Solution, press the soft keys under ***METHOD OPTIONS, (MORE)*** then ***STD: OFF***. Press **ENTER** to accept the default concentration, the value of which will depend on the selected units. If an alternate concentration is used, enter the actual concentration and press **ENTER** to return to the read screen. See Section *1.5.5 Adjusting the Standard Curve* for more information.

Method Performance

Precision

Standard: 1.000 mg/L Fe

Program	95% Confidence Limits
2150	0.997–1.003 mg/L Fe
2155	0.997–1.003 mg/L Fe

For more information on determining precision data and method detection limits, refer to Section *1.5*.

Estimated Detection Limit

Program	EDL
2150	0.008 mg/L Fe
2155	0.007 mg/L Fe

For more information on derivation and use of Hach's estimated detection limit, see Section *1.5.2*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, Appendix B, see Section *1.5.1*.

Sensitivity
Program Number: 2150

Portion of Curve:	ΔAbs	ΔConcentration
Entire Range	0.010	0.0210 mg/L

Program Number: 2155

Portion of Curve:	ΔAbs	ΔConcentration
Entire Range	0.010	0.0226 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

Preparing ferrous standards is difficult. These standards are very unstable and degrade rapidly. Only a trained chemist should prepare these standards.

To perform an ferrous iron calibration using the 1,10 phenanthroline method, prepare calibration standards containing 0.50, 1.00, 2.00, and 3.00 mg/L ferrous iron as follows:

a. Prepare a 100 mg/L ferrous iron stock solution by dissolving 0.7022 grams of Ferrous Ammonium Sulfate, hexahydrate, in deionized water. Dilute to one liter in a Class A volumetric flask. Stopper and invert several times to mix. Prepare this solution just before use.

b. Into four different 100-mL Class A volumetric flasks, pipet 0.50, 1.00, 2.00 and 3.00 mL of the 100-mg/L ferrous iron stock solution. Dilute each flask to volume with deionized water. Stopper and invert each flask to mix. Prepare these standards just before use.

c. Using the 1,10 phenanthroline method and the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standards prepared above.

Summary of Method

The 1,10 phenanthroline indicator in the Ferrous Iron Reagent reacts with ferrous iron in the sample to form an orange color in proportion to the iron concentration. Ferric iron does not react. The ferric iron (Fe^{3+}) concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to Section *1*.

Pollution Prevention and Waste Management

For information on pollution prevention and waste management, refer to Section *1*.

REQUIRED REAGENTS AND STANDARDS (Using Powder Pillows)

Description	Quantity Required per test	Unit	Cat. No.
Ferrous Iron Reagent Powder Pillows	1 pillow	100/pkg	1037-69

REQUIRED REAGENTS AND STANDARDS (Using AccuVac Ampuls)

Ferrous Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25140-25

REQUIRED EQUIPMENT AND SUPPLIES (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968-00
DR/4000 1-Inch Cell Adapter	1	each	48190-00

REQUIRED EQUIPMENT AND SUPPLIES (Using AccuVac Ampuls)

Beaker, 50-mL	1	each	500-41
DR/4000 AccuVac Ampul Adapter	1	each	48187-00
Sample Cell, 10-mL, with cap (zeroing vial)	1	each	21228-00

OPTIONAL REAGENTS AND STANDARDS

Ferrous Ammonium Sulfate, hexahydrate, ACS	113 g	11256-14
Water, deionized	4 liters	272-56

OPTIONAL EQUIPMENT AND SUPPLIES

AccuVac Snapper	each	24052-00
Balance, electronic, 110 VAC	each	26104-00
Balance, electronic, 220 VAC	each	26104-02
Clippers, shears, 7 ¼-inch	each	23694-00
DR/4000 Carousel Module Kit	each	48070-02
DR/4000 Flow Cell Module Kit, 1-inch	each	48070-04
DR/4000 Flow Cell Module Kit, 1-cm	each	48070-05
DR/4000 Sipper Module Kit, 1-inch	each	48070-03
Flask, volumetric, 100-mL, Class A	each	14574-42
Flask, volumetric, 1000-mL, Class A, with stopper	each	14574-53
pH Meter, *sens**ion**™1*, portable	each	51700-00
pH Paper, pH 1.0 to 11.0	5 rolls/pkg	391-33
Pipet, volumetric, 0.50-mL, Class A	each	14515-34
Pipet, volumetric, 1.00-mL, Class A	each	14515-35
Pipet, volumetric, 2.00-mL, Class A	each	14515-36
Pipet, volumetric, 3.00-mL, Class A	each	14515-03
Pipet Filler, safety bulb	each	14651-00

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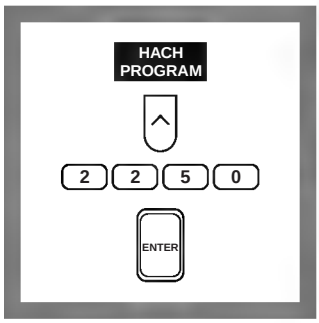
MANGANESE

✔ **Method 8034** **Periodate Oxidation Method***

HR (0 to 20.0 mg/L)

Scope and Application: *For soluble manganese in water and wastewater; USEPA approved for reporting wastewater analyses (digestion is required)**. See Section 1 for digestion procedure. The estimated detection limit for program number 2250 is 0.1 mg/L as Mn.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater*
** *Federal Register,* 44 (116) 34193 (June 14, 1979)



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for high range manganese (Mn) by pressing **2250** with the numeric keys.

Press: **ENTER**

Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation, following these steps. Adjust pH of preserved samples before analysis.*

Note: *The Flow Cell and Sipper Modules can be used with this procedure. Use a 25-mL sample and reagents with the Flow Cell Module.*

2. The display will show:

HACH PROGRAM: 2250
Manganese, HR

The wavelength (λ), **525 nm**, is automatically selected.

3. Fill a cell with 10 mL of sample.

Note: *For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3 through 10, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under* ***ZERO****. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE)****, and then* ***BLANK:OFF****. Enter the reagent blank value and press* **ENTER***. Repeat for each new lot of reagent.*

Note: *For proof of accuracy, use a 5.0 mg/L manganese standard solution (preparation given in the Accuracy Check* section*) in place of the sample.*

4. Add the contents of one Buffer Powder Pillow, Citrate Type for Manganese. Swirl to mix.

5. Add the contents of one Sodium Periodate Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

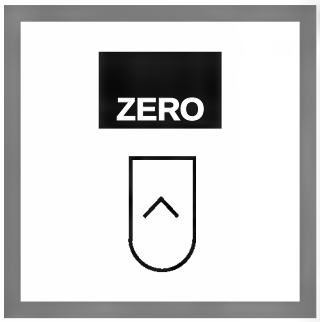
Note: *A violet color will develop if manganese is present.*

6. Press the soft key under ***START TIMER***.

A 2-minute reaction period will begin.

7. Fill another sample cell (the blank) with 10 mL of sample.

8. When the timer beeps, place the blank into the cell holder. Close the light shield.



9. Press the soft key under ***ZERO***.

The display will show:

0.0 mg/L Mn

Note: *If you are using a reagent blank correction, the display will show the correction.*

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

10. Within eight minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield. The result in mg/L Mn (or chosen units) will be displayed.

Note: *Results may be expressed as permanganate (MnO_4^-) or as potassium permanganate ($KMnO_4$). Press the soft keys under* ***OPTIONS*** *and then* ***FORM:*** *to scroll through the available options.*

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Interfering Substance	Interference Levels and Treatments
Calcium	700 mg/L
Chloride	70,000 mg/L
Iron	5 mg/L
Magnesium	100,000 mg/L
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see Section *1.3.1 pH Interference.*

Sample Collection, Storage and Preservation

Collect samples in acid-washed plastic bottles. Do not use glass containers due to possible adsorption of Mn to glass. If samples are acidified, adjust the pH to 4–5 with 5.0 N Sodium Hydroxide before analysis. Do not exceed pH 5, as manganese may precipitate. Correct the test result for volume additions; see Section *1.2.2 Correcting for Volume Additions*.

If only dissolved manganese is to be determined, filter the sample before acid addition.

Accuracy Check

Standard Additions Method

a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under ***OPTIONS, (MORE)*** and then ***STD ADD***.

b. Press **ENTER** to accept the default sample volume (mL), 10.

c. Press **ENTER** to accept the default standard concentration (mg/L), 100.

d. Press the soft key under ***ENTRY DONE***.

e. Prepare a 10.0-mg/L manganese standard solution. (See *Calibration Standard Preparation*)

f. Use the TenSette Pipet to add 0.1, 0.2 mL and 0.3 mL of standard, respectively to three 10-mL samples and mix each thoroughly.

g. Analyze each standard addition sample as described above. Accept the standard additions reading by pressing the soft key under ***READ*** each time. Each addition should reflect approximately 100% recovery.

h. After completing the sequence, the display will show the extrapolated concentration value and the “best-fit” line through the standard additions data points, accounting for matrix interferences.

i. See Section *1.4.1 Standard Additions* for more information.

Standard Solution Method

Prepare a 10.0-mg/L manganese standard solution by pipetting 10.0 mL of Manganese Standard Solution, 1000-mg/L, into a 1000-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution daily. Perform the manganese periodate oxidation procedure as described above.

The calibration curve can be adjusted to account for variability in laboratory technique. To adjust the calibration curve using the reading obtained with the 10.0Hmg/L standard solution, press the soft keys under ***OPTIONS, (MORE)*** then ***STD: OFF***. Press **ENTER** to accept the default concentration, the value of which will depend on the selected units. If an alternate concentration is used, enter the actual concentration and press **ENTER** to return to the read screen. See Section *1.5.5 Adjusting the Standard Curve* for more information.

Method Performance

Precision

Standard: 10.0 mg/L Mn

Program	95% Confidence Limits
2250	9.9–10.1 mg/L Mn

For more information on determining precision data and method detection limits, refer to Section *1.5*.

Estimated Detection Limit

Program	EDL
2250	0.1 mg/L Mn

For more information on derivation and use of Hach's estimated detection limit, see Section *1.5.2*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see Section *1.5.1*.

Sensitivity

Program Number: 2250

Portion of Curve	ΔAbs	ΔConcentration
0.010 Abs	0.010	0.11 mg/L
10 mg/L	0.010	0.13 mg/L
18 mg/L	0.010	0.14 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a manganese calibration using the periodate oxidation method, prepare a 100-mg/L Mn stock solution by pipetting 10.00 mL of a 1000-mg/L Manganese Standard Solution (Cat. No. 12791-42) into a 100-mL volumetric flask using Class A glassware. Dilute to the mark with deionized water and mix thoroughly.

Prepare calibration standards containing 2.0, 4.0, 8.0, 12.0, 16.0 and 20.0 mg/L Mn as follows:

a. Into six different 100-mL volumetric flasks, pipet 2.00, 4.00, 8.00, 12.00, 16.00 and 20.00 mL of the 100-mg/L Mn stock solution using Class A glassware.

b. Dilute to the mark with deionized water. Mix thoroughly.

c. Using the periodate oxidation method and the calibration procedure described above, generate a calibration curve from the standards prepared above.

Summary of Method

Manganese in the sample is oxidized to the purple permanganate state by sodium periodate, after buffering the sample with citrate. The purple color is directly proportional to the manganese concentration.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to Section *1*.

Pollution Prevention and Waste Management

For information on pollution prevention and waste management, refer to Section *1*.

REQUIRED REAGENTS AND STANDARDS

	Cat. No.
High Range Manganese Reagent Set (100 Tests*)	24300-00
Includes: (1) 21076-69, (1) 21077-69	

Description	Quantity Required per test	Unit	Cat. No.
Buffer Powder Pillows, citrate type for manganese	1 pillow	100/pkg	21076-69
Sodium Periodate Powder Pillows, for manganese	1 pillow	100/pkg	21077-69

REQUIRED EQUIPMENT AND SUPPLIES

DR/4000 1-Inch Cell Adapter	1	each	48190-00

OPTIONAL REAGENTS AND STANDARDS

Hydrochloric Acid, 6.0 N	500 mL	884-49
Manganese Standard Solution, 1000-mg/L Mn	100 mL	12791-42
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Solution, 5.0 N	100 mL MDB	2450-32
Water, deionized	4 liters	272-56

OPTIONAL EQUIPMENT AND SUPPLIES

Ampule Breaker Kit	each	21968-00
Dropper, 0.5 and 1.0 mL marks	20/pkg	21247-20
DR/4000 Carousel Module Kit	each	48070-02
DR/4000 Flow Cell Module Kit, 1-inch	each	48070-04
DR/4000 Flow Cell Module Kit, 1-cm	each	48070-05
DR/4000 Sipper Module Kit, 1-inch	each	48090-03
Flask, Erlenmeyer, 250-mL	each	505-46
Flask, volumetric, Class A, 50-mL	each	14574-41
Flask, volumetric, Class A, 100-mL	each	14574-42
Flask, volumetric, Class A, 1000-mL	each	14574-53
pH Paper, pH 1.0 to 11.0	5 rolls/pkg	391-33
pH Meter, *sens**ion**™1*, portable	each	51700-00
Pipet, serological, 1-mL	each	532-35
Pipet, serological, 5-mL	each	532-37
Pipet, volumetric, Class A, 2.00-mL	each	14515-36
Pipet, volumetric, Class A, 4.00-mL	each	14515-04
Pipet, volumetric, Class A, 5.0-mL	each	14515-37
Pipet, volumetric, Class A, 6.0-mL	each	14515-06
Pipet, volumetric, Class A, 8.0-mL	each	14515-08
Pipet, volumetric, Class A, 10.0-mL	each	14515-38
Pipet, volumetric, Class A, 20.0-mL	each	14515-20
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Filler, safety bulb	each	14651-00

* 100 tests equal 100 samples and 100 blanks.

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NITROGEN, Ammonia

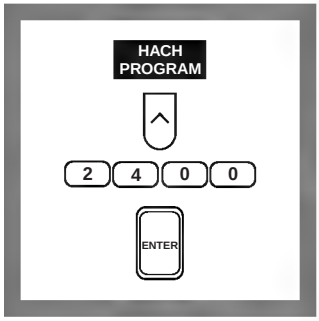
✔ **Method 8038**

Nessler Method*

(0 to 2.500 mg/L NH_3–N)

Scope and Application: *For water, wastewater, seawater; distillation is required for wastewater and seawater; USEPA accepted for wastewater analyses (distillation is required). See Distillation following this procedure. The estimated detection limit for program number 2400 is 0.017 mg/L.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater 4500-NH_3 B & C.*



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program for low range ammonia nitrogen (NH_3-N) by pressing **2400** with the numeric keys.

Press: **ENTER**

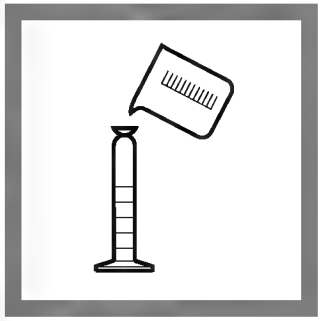
Note: *If samples cannot be analyzed immediately, see Sample collection, Storage and Preservation following these steps. Adjust the pH of preserved samples before analysis.*

Note: *The Flow Cell and Sipper Modules can be used with this procedure. Periodically clean the cells by pouring a few sodium thiosulfate pentahydrate crystals into the cell funnel. Flush it through the funnel and cell with enough deionized water to dissolve. Rinse out the crystals.*

2. The display will show:

HACH PROGRAM: 2400 N, Ammonia Nessler

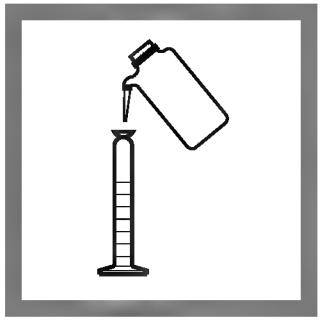
The wavelength (λ), **425 nm**, is automatically selected.



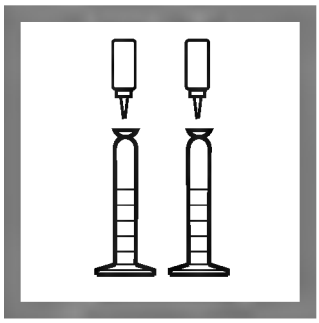
3. Fill a 25-mL mixing graduated cylinder (the prepared sample) to the 25-mL mark with sample.

Note: *For proof of accuracy, use a 1.0-mg/L Ammonia Nitrogen Standard Solution (listed under OPTIONAL REAGENTS AND STANDARDS) in place of the sample.*

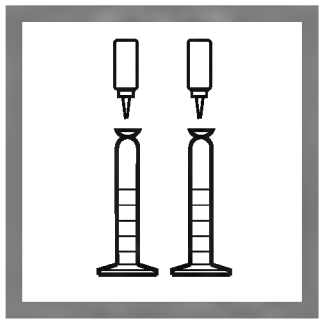
Note: *For non-preserved samples with extreme pH, see the Interferences section.*



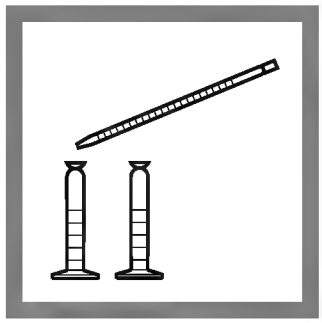
4. Fill another 25-mL mixing graduated cylinder (the blank) with deionized water.



5. Add three drops of Mineral Stabilizer to each cylinder. Stopper. Invert several times to mix.



6. Add three drops of Polyvinyl Alcohol Dispersing Agent to each cylinder by holding the dropping bottle vertically. Invert several times to mix.



7. Pipet 1.0 mL of Nessler Reagent into each cylinder. Stopper. Invert several times to mix.

Note: *Nessler Reagent is toxic and corrosive. Pipet carefully and use a pipet filler.*

Note: *A yellow color will develop if ammonia is present. (The reagent will cause a faint yellow color in the blank.)*

Note: *Do not wait more than 15 minutes after reagent addition (Step 7) before performing Step 12.*

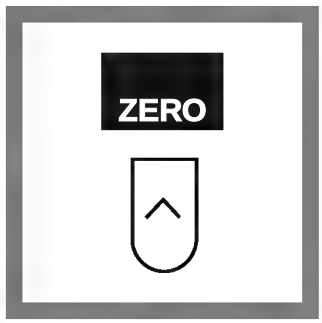
8. Press the soft key under ***START TIMER***.

A one-minute reaction period will begin.

Note: *Continue with Step 9 while timer is running.*

9. Pour each solution into a sample cell.

10. When the timer beeps, place the blank into the cell holder. Close the light shield.



11. Press the soft key under ***ZERO***.

The display will show:

0.000 mg/L N NH_3

Note: *For alternate concentration units press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

12. Place the prepared sample into the cell holder. Close the light shield. Results in mg/L ammonia expressed as nitrogen (NH_3–N) (or chosen units) will be displayed.

Note: *The results may be expressed as mg/L ammonia (NH_3) or mg/L ammonium (NH_4^+). Press the soft keys under* ***OPTIONS****, then* ***FORM:*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

Interferences

Interfering Substance	Interference Levels and Treatments
Chlorine	Remove residual chlorine by adding 2 drops of sodium arsenite for each mg/L Cl from a 250 mL sample. Sodium thiosulfate can be used in place of sodium arsenite. See *Sample collection, Storage and Preservation* below.
Hardness	A solution containing a mixture of 500 mg/L $CaCO_3$ and 500 mg/L Mg as $CaCO_3$ does not interfere. If the hardness concentration exceeds these concentrations, add extra Mineral Stabilizer.
Iron	Interferes at all levels by causing turbidity with Nessler Reagent.
Seawater	May be analyzed by adding of 1.0 mL (27 drops) of Mineral Stabilizer to the sample before analysis. This complexes the high magnesium concentrations found in sea water, but the sensitivity of the test is reduced by 30 percent due to the high chloride concentration. For best results, perform a calibration, using standards spiked to the equivalent chloride concentration, or distill the sample as described below.
Sulfide	Interferes at all levels by causing turbidity with Nessler Reagent.
Glycine, various aliphatic and aromatic amines, organic chloramines, acetone, aldehydes and alcohols	May cause greenish or other off colors or turbidity. Distill the sample if these compounds are present.

Sample collection, Storage and Preservation

Collect samples in clean glass or plastic bottles. If chlorine is present, add one drop of 0.1 N Sodium Thiosulfate for each 0.3 mg/L Cl_2 in a 1-liter sample. Preserve the sample by reducing the pH to 2 or less with sulfuric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Warm samples to room temperature and neutralize with 5 N Sodium Hydroxide before analysis. Correct the test result for volume additions; see Section *1.2.2 Correcting for Volume Additions*.

Accuracy Check

Standard Additions Method

a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under ***OPTIONS, (MORE)*** and then ***STD ADD***.

b. Press **ENTER** to accept the default sample volume (mL), 25.

c. Press **ENTER** to accept the default standard concentration (mg/L), 50.

d. Press the soft key under ***ENTRY DONE***.

e. Snap the neck off a Nitrogen Ammonia Voluette Ampule Standard, 50-mg/L NH_3–N.

f. Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively to three 25-mL samples and mix each thoroughly.

g. Analyze each standard addition sample as described above. Accept the standard additions reading by pressing the soft key under ***READ*** each time. Each addition should reflect approximately 100% recovery.

h. After completing the sequence, the display will show the extrapolated concentration value and the “best-fit” line through the standard additions data points, accounting for matrix interferences.

i. See Section *1.4.1 Standard Additions* for more information.

Standard Solutions Method
To check accuracy, use a 1.0-mg/L Nitrogen Ammonia Standard Solution listed under *OPTIONAL REAGENTS AND STANDARDS*. Or, prepare a 1.0-mg/L ammonia nitrogen standard solution by pipetting 1.00 mL of Nitrogen Ammonia Voluette Ampule Standard, 50-mg/L, into a 50-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution daily. Perform the Nessler procedure as described above.

To adjust the calibration curve using the reading obtained with the 1.0-mg/L Nitrogen Ammonia Standard Solution, press the soft keys under ***OPTIONS, MORE*** then ***STD: OFF***. Press **ENTER** to accept the displayed concentration, the value of which depends on the selected units. If an alternate concentration is used, enter the actual concentration and press **ENTER** to return to the read screen. See Section *1.5.5 Adjusting the Standard Curve* for more information.

Method Performance

Precision
Standard: 1.00 mg/L NH_3–N

Program	95% Confidence Limits
2400	0.99–1.01 mg/L NH_3–N

For more information on determining precision data and method detection limits, refer to Section *1.5*.

Estimated Detection Limit

Program	EDL
2400	0.017 mg/L NH_3–N

For more information on derivation and use of Hach's estimated detection limit, see Section *1.5.2*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, Appendix B, see Section *1.5.1*.

Sensitivity
Program Number: 2400

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	0.01717 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Distillation

a. Measure 250 mL of sample into a 250-mL graduated cylinder and pour into a 400-mL beaker. Destroy chlorine, if necessary, by adding 2 drops of Sodium Arsenite Solution per mg/L Cl_2.

b. Add 25 mL of Borate Buffer Solution and mix. Adjust the pH to about 9.5 with 1 N Sodium Hydroxide solution. Use a pH meter.

c. Set up the general purpose distillation apparatus as shown in the *Hach Distillation Apparatus Manual*. Pour the solution into the distillation flask. Add a stir bar.

d. Use a graduated cylinder to measure 25 mL of deionized water into a 250-mL erlenmeyer flask. Add the contents of one Boric Acid Powder Pillow. Mix thoroughly. Place the flask under the still drip tube. Elevate so the end of the tube is immersed in the solution.

e. Turn on the heater power switch. Set the stir control to 5 and the heat control to 10. Turn on the water and adjust to maintain a constant flow through the condenser.

f. Turn off the heater after collecting 150 mL of distillate. Immediately remove the collection flask to avoid sucking solution into the still. Measure the distillate to ensure 150 mL was collected (total volume = 175 mL).

g. Adjust the pH of the distillate to about 7 with 1 N Sodium Hydroxide. Use a pH meter.

h. Pour the distillate into a 250-mL volumetric flask; rinse the erlenmeyer with deionized water. Add the rinsings to the volumetric. Dilute to the mark. Stopper. Mix thoroughly. Analyze as described above.

Calibration Standard Preparation

To perform an ammonia calibration using the Nessler method, prepare standards containing 0.5, 1.0 and 2.0 mg/L ammonia-nitrogen as follows:

a. Into three different 100-mL volumetric flasks pipet 0.5, 1.0 and 2.0 mL of the 100-mg/L Nitrogen Ammonia Standard Solution (Cat No. 24065-49) using Class A glassware.

b. Dilute to the mark with deionized ammonia-free water. Mix thoroughly.

c. Using the Nessler method and the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standard prepared above.

Summary of Method

The Mineral Stabilizer complexes hardness in the sample. The Polyvinyl Alcohol Dispersing Agent aids the color formation in the reaction of Nessler Reagent with ammonium ions. A yellow color is formed proportional to the ammonia concentration.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to Section *1*.

Pollution Prevention and Waste Management

Nessler Reagent contains mercuric iodide. Both the sample and the blank will contain mercury (D009) at a concentration regulated as a hazardous waste by the Federal RCRA. Do not pour these solutions down the drain. See Section *1* for further information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS

Ammonia Nitrogen Reagent Set 24582-00
Includes: (1) 21194-49, (1) 23766-26, (1) 23765-26

Description	Quantity Required Per Test	Unit	Cat. No.
Nessler Reagent	2 mL	500 mL	21194-49
Mineral Stabilizer	6 drops	50 mL*	SCDB 23766-26
Polyvinyl Alcohol Dispersing Agent	6 drops	50 mL	SCDB 23765-26
Water, deionized	25 mL	4 liters	272-56

REQUIRED EQUIPMENT AND SUPPLIES

Cylinder, graduated, mixing, 25-mL	2	each	21190-40
DR/4000 1-Inch Cell Adapter	1	each	48190-00
Pipet, serological, 1-mL	2	each	532-35
Pipet Filler, safety bulb	1	each	14651-00

OPTIONAL REAGENTS AND STANDARDS

Borate Buffer Solution	1000 mL		14709-53
Boric Acid Powder Pillows	50/pkg		14817-66
Nitrogen, Ammonia Standard Solution, 1-mg/L NH_3-N	500 mL		1891-49
Nitrogen, Ammonia Standard Solution, 100-mg/L NH_3–N	500 mL		24065-49
Nitrogen, Ammonia Standard Solution, 0-mL Voluette Ampule, 50-mg/L NH_3–N	16/pkg		14791-10
Sodium Arsenite Solution, 5.0-g/L	100 mL	MDB	1047-32
Sodium Hydroxide Standard Solution, 5.0 N	100 mL*	MDB	2450-32
Sodium Hydroxide Standard Solution, 1.0 N	100 mL*	MDB	1045-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL*	MDB	323-32
Sulfuric Acid, ACS, concentrated	500 mL*		979-49

* Contact Hach for larger sizes.

OPTIONAL EQUIPMENT AND SUPPLIES

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Beaker, 400-mL	each	500-48
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 250-mL	each	508-46
Distillation Apparatus, general purpose accessories	each	22653-00
Distillation heater and support apparatus set, 115 VAC	each	22744-00
Distillation heater and support apparatus set, 230 VAC	each	22744-02
Dropper, plastic, 0.5- and 1.0-mL marks	10/pkg	21247-10
DR/4000 Carousel Module Kit	each	48070-02
DR/4000 Flow-Thru Cell Module	each	48090-04
DR/4000 Sipper Cell Module, 1-inch	each	48090-03
Flask, Erlenmeyer, 250-mL	each	505-46
Flask, volumetric, 50-mL	each	547-41
Flask, volumetric, 250-mL	each	547-46
pH Meter, *sens**ion***™*1*, portable	each	51700-00
Pipet, serological, 2-mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1-mL	each	14515-35
Thermometer, -10 to 110 °C	each	1877-01

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HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

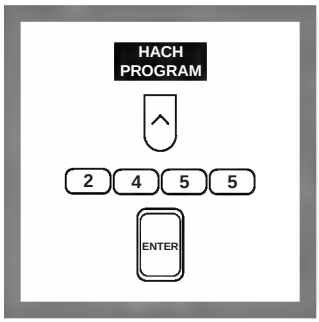
NITROGEN, Ammonia

Method 8155 **Salicylate Method***

Powder Pillows **(0 to 0.80 mg/L NH_3–N)**

Scope and Application: *For water, wastewater, and seawater.*
The estimated detection limit for program number 2455 is 0.09 mg/L NH_3–N.

* Adapted from *Clin. Chim. Acta.*, *14,* 403 (1966)



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for ammonia nitrogen (NH_3–N) by pressing **2455** with the numeric keys.

Press: **ENTER**

Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps.*

Note: *The Flow Cell and Sipper Modules can be used with this procedure.*

2. The display will show:

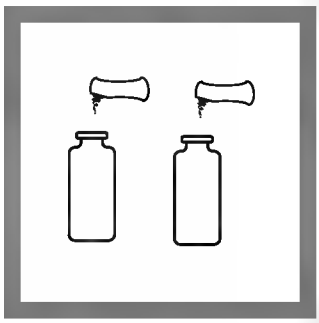
HACH PROGRAM: 2455 N, Ammonia Salic.

The wavelength (λ), **655 nm**, is automatically selected.

3. Fill a glass-stoppered sample cell to the 25-mL mark with sample.

Note: *For proof of accuracy, a 0.60-mg/L NH_3–N solution (preparation given in the Accuracy Check section) can be used in place of the sample.*

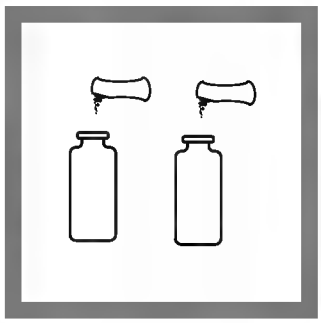
4. Fill another glass-stoppered sample cell to the 25-mL mark with deionized water (the blank).



5. Add the contents of one Ammonia Salicylate Powder Pillow to each cell. Stopper and shake to dissolve the powder.

6. Press the soft key under ***START TIMER***.

A 3-minute reaction period will begin.



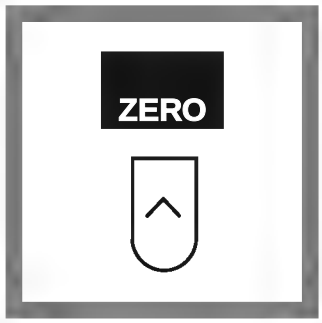
7. When the timer beeps, add the contents of one Ammonia Cyanurate Reagent Powder Pillow to each cell.
Stopper and shake to dissolve the reagent.

8. Press the soft key under ***START TIMER***.

A 15-minute reaction period will begin.

Note: *A green color will develop if ammonia nitrogen is present.*

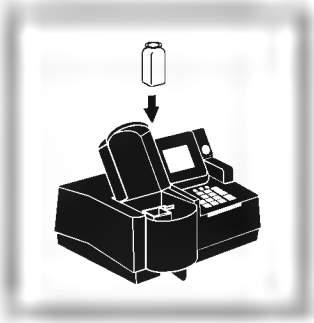
9. When the timer beeps, place the blank into the cell holder. Close the light shield.



10. Press the soft key under ***ZERO***.

The display will show:

0.00 mg/L NH_3–N



11. Place the prepared sample into the cell holder. Close the light shield. Result in mg/L ammonia as nitrogen (NH_3–N) (or chosen units) will be displayed.

Note: *Results may be expressed as mg/L ammonia (NH_3) or mg/L ammonium (NH_4^+). Press the soft keys under* ***OPTIONS****, then* ***FORM:*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

Interferences

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels
Calcium	Greater than 1000 mg/L as $CaCO_3$
Iron	All levels. Correct for iron interference as follows: **1.** Determine the amount of iron present in the sample by following one of the Iron, Total, procedures. **2.** Add the same iron concentration to the ammonia-free water in Step 3. The interference will be successfully blanked out.
Magnesium	Greater than 6000 mg/L as $CaCO_3$
Nitrate	Greater than 100 mg/L as NO_3^--N
Nitrite	Greater than 12 mg/L as NO_2^--N
Phosphate	Greater than 100 mg/L as PO_4^{3-}-P
Sulfate	Greater than 300 mg/L as SO_4^{2-}
Sulfide	Sulfide will intensify the color. Eliminate sulfide interference as follows: **1.** Measure about 350 mL of sample in a 500-mL erlenmeyer flask. **2.** Add the contents of one Sulfide Inhibitor Reagent Powder Pillow. Swirl to mix. **3.** Filter the sample through a folded filter paper. **4.** Use the filtered solution in Step 3.
Other Substances	Less common interferences such as **hydrazine** and **glycine** will cause intensified colors in the prepared sample. **Turbidity** and **color** will give erroneous high values. Samples with severe interferences require distillation. Hach recommends the distillation procedure using the Hach General Purpose Distillation Set. See *OPTIONAL REAGENTS AND STANDARDS.*

Sample Collection, Storage and Preservation

Collect samples in clean plastic or glass bottles. Most reliable results are obtained when samples are analyzed as soon as possible after collection.

If chlorine is known to be present, the sample must be treated immediately with sodium thiosulfate. Add one drop of Sodium Thiosulfate Standard Solution, 0.1 N, for each 0.3 mg of chlorine present in a one-liter sample.

For longer storage, adjust the pH to 2 or less with concentrated sulfuric acid (about 2 mL per liter). Store samples at 4 °C or less. Samples preserved in this manner can be stored up to 28 days. Just before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution. Correct the test result for volume additions; see Section *1.2.2 Correcting for Volume Additions*.

Accuracy Check

Standard Additions Method

a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under ***OPTIONS, (MORE)*** and then ***STD ADD***.

b. Press **ENTER** to accept the default sample volume (mL), 25.

c. Press **ENTER** to accept the default standard concentration (mg/L), 10.

d. Press the soft key under ***ENTRY DONE***.

e. Open an Ammonia Nitrogen Standard Solution, 10-mg/L as NH_3–N.

f. Use the TenSette Pipet to add 0.2 mL, 0.4 mL and 0.6 mL of standard, respectively to three 25-mL samples and mix each thoroughly.

g. Analyze each standard addition sample as described above. Accept the standard addition reading by pressing the soft key under ***READ*** each time. Each addition should reflect approximately 100% recovery.

h. After completing the sequence, the display will show the extrapolated concentration value and the “best-fit” line through the standard additions data points, accounting for matrix interferences.

i. See Section *1.4.1 Standard Additions* for more information.

Standard Solution Method

Prepare a 0.60-mg/L ammonia nitrogen standard by diluting 6.00 mL of the Ammonia Nitrogen Standard Solution, 10-mg/L, to 100 mL with deionized water. Or, using the TenSette Pipet, prepare a 0.60-mg/L ammonia nitrogen standard by diluting 1.2 mL of a Ammonia Nitrogen Voluette Standard Solution, 50-mg/L as NH_3-N, to 100 mL with deionized water.

To adjust the calibration curve using the reading obtained with the 0.60-mg/L standard solution, press the soft keys under ***OPTIONS, MORE*** then ***STD: OFF***. Press **ENTER** to accept the displayed concentration, the value of which depends on the selected units. If an alternate concentration is used, enter the actual concentration and press **ENTER** to return to the read screen. See Section *1.5.5 Adjusting the Standard Curve* for more information.

Method Performance

Precision
Standard: 0.60 mg/L NH_3–N

Program	95% Confidence Limits
2455	0.54–0.66 mg/L NH_3–N

For more information on determining precision data and method detection limits, refer to Section *1.5*.

Estimated Detection Limit

Program	EDL
2455	0.09 mg/L NH_3–N

For more information on derivation and use of Hach's estimated detection limit, see Section *1.5.2*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see Section *1.5.1*.

Sensitivity
Program Number: 2455

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	0.004 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform an nitrogen calibration using the salicylate method, prepare a 10 mg/L ammonia nitrogen stock solution by pipetting 10 mL of a 100-mg/L Nitrogen Ammonia Standard Solution (Cat. No. 24065-49) into a 100-mL volumetric flask using Class A glassware. Dilute to the mark with deionized water and mix thoroughly. Or use the 10 mg/L Nitrogen Ammonia Standard Solution from Hach (Cat. No. 153-49).

Prepare calibration standards containing 0.20, 0.50, and 0.80 mg/L ammonia nitrogen as follows:

a. Into three different 100-mL volumetric flasks, pipet 2.00, 5.00, and 8.00 mL of the 10-mg/L Nitrogen Ammonia Standard Solution using Class A glassware.

b. Dilute to the mark with deionized water. Mix thoroughly.

c. Using the salicylate method and the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standards prepared above.

Summary of Method

Ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to Section *1*.

Pollution Prevention and Waste Management

For information on pollution prevention and waste management, refer to Section *1*.

REQUIRED REAGENTS AND STANDARDS

Description	Cat. No
Ammonia Nitrogen Reagent Set, (100 tests)	22437-00
Includes: (4) 23955-66, (4) 23953-66	

Description	Quantity Required Per Test	Unit	Cat. No.
Ammonia Cyanurate Reagent Powder Pillows	2	25/pkg	23955-66
Ammonia Salicylate Reagent Powder Pillows	2	25/pkg	23953-66

REQUIRED EQUIPMENT AND SUPPLIES

Description	Quantity Required Per Test	Unit	Cat. No.
Clippers, for opening powder pillows	1	each	968-00
DR/4000 1-Inch Cell Adapter	1	each	48190-00
Sample Cells, matched pair, 1 inch, w/ stopper	2	pair	26126-02

OPTIONAL REAGENTS AND STANDARDS

Ammonia Nitrogen Standard Solution, 10-mg/L as NH_3–N		500 mL	153-49
Ammonia Nitrogen Standard Solution, 10-mL Voluette Ampule, 50-mg/L as NH_3–N		16/pkg	14791-10
Ammonia Nitrogen Standard Solution, 100-mg/L as NH_3–N		500 mL	24065-49
Sodium Hydroxide Standard Solution, 1.00 N		100 mL MDB	1045-32
Sodium Hydroxide Standard Solution, 5.0 N		59 mL DB	2450-26
Sodium Thiosulfate Standard Solution, 0.1 N		100 mL MDB	323-32
Sulfide Inhibitor Reagent Powder Pillows		100/pkg	2418-99
Sulfuric Acid, concentrated, ACS		500 mL	979-49
Sulfuric Acid Standard Solution, 1.000 N		100 mL MDB	1270-32
Water, deionized		4 liters	272-56

OPTIONAL EQUIPMENT AND SUPPLIES

Cylinder, graduated, polypropylene, 500-mL	each	1081-49
Distillation Heater and Support Apparatus, 115 VAC	each	22744-00
Distillation Heater and Support Apparatus, 230 VAC	each	22744-02
Distillation Apparatus Set, general purpose	each	22653-00
DR/4000 Carousel Module Kit	each	48070-02
DR/4000 Flow Cell Module Kit, 1-inch	each	48070-04
DR/4000 Flow Cell Module Kit, 1-cm	each	48070-05
DR/4000 Sipper Module Kit, 1-inch	each	48090-03
Filter Paper, folded, 12.5-cm	100	1894-57
Flask, Erlenmeyer, polypropylene, 500-mL	each	1082-49
Flask, volumetric, Class A, 100-mL	each	14574-42
Funnel, poly, 65-mm	each	1083-67
pH Meter, *sens**ion***™*1*, portable	each	517000-00
Pipet Filler, safety bulb	each	14651-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 2.00-mL	each	14515-36
Pipet, volumetric, Class A, 5.00-mL	each	14515-37
Pipet, volumetric, Class A, 6.00-mL	each	14515-06
Pipet, volumetric, Class A, 8.00-mL	each	14515-08
Thermometer, -10 to 110 °C	each	1877-01

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Carbon Dioxide

Method 8205 — **Digital Titrator Method Using Sodium Hydroxide**

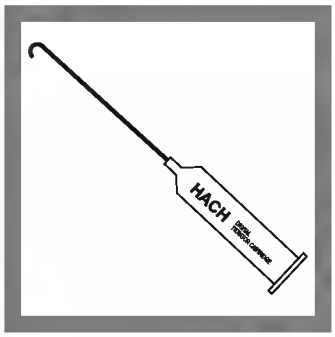
Digital Titrator — **(10 to 1000 mg/L as CO_2)**

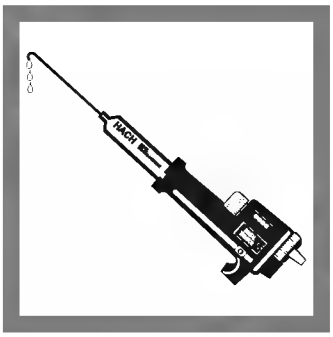
Scope and Application: For water and seawater

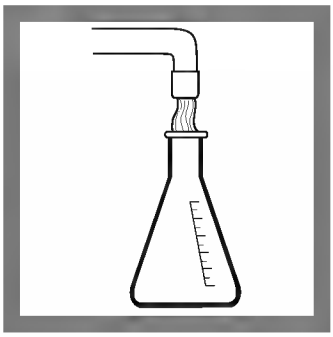
Tips and Techniques

- For added convenience when stirring, use the TitraStir apparatus (Cat. No. 19400-00, -10).
- For more accurate results, check the calibration of the Erlenmeyer flask. Fill a graduated cylinder with the sample volume of deionized water. Pour the water into the Erlenmeyer flask and mark the proper level with a wax pencil or permanent marker.
- Four drops of Phenolphthalein Indicator Solution (Cat. No. 162-32) can be substituted for the Phenolphthalein Indicator Powder Pillow.
- Minimize agitation of the sample to avoid loss of carbon dioxide.

Digital Titration — Method 8205





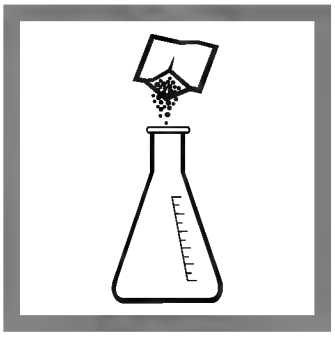


1. Select a sample size and a Sodium Hydroxide (NaOH) Titration Cartridge in *Table 1* that correspond to the expected carbon dioxide (CO_2) concentration.

2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.

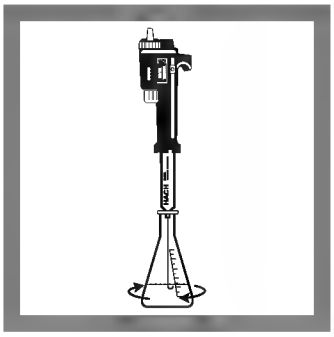
3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

4. Collect a water sample directly into the titration flask by filling to the appropriate mark.



5. Add the contents of one Phenolphthalein Indicator Powder Pillow and mix.

If a pink color forms, no carbon dioxide is present.



6. Place the delivery tube into the solution and swirl the flask gently while titrating with sodium hydroxide from colorless to a light pink color that persists for 30 seconds (pH 8.3). Record the number of digits required.

7. Calculate:

Total Digits Required x Digit Multiplier = mg/L as CO_2

Table 1

Range (mg/L as CO_2)	Sample Volume (mL)	Titration Cartridge (N NaOH)	Catalog Number	Digit Multiplier
10–50	200	0.3636	14378-01	0.1
20–100	100	0.3636	14378-01	0.2
100–400	200	3.636	14380-01	1.0
200–1000	100	3.636	14380-01	2.0

Interferences

Highly colored or turbid sample may mask the color change of the end point. Use a pH meter (Cat. No. 51700-10) for these samples, titrating to pH 8.3. Other acid components in the sample will be titrated and interfere directly in this determination.

Sodium hydroxide standard solutions tend to lose strength slowly with age and should be checked periodically by titrating a known standard. Check the solution frequently (monthly) by titrating 50 mL of Potassium Acid Phthalate Standard Solution, 100 mg/L CO_2, using Phenolphthalein Indicator Solution. The titration should require 5.00 mL of titrant. If the volume required for this titration is greater than 5.25 mL, discard the sodium hydroxide and replace it with a fresh supply.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples as soon as possible after collection. If immediate analysis is not possible, the samples may be stored for at least 24 hours by cooling to 4 °C (39 °F) or below. Before analysis, warm the samples to room temperature.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Carbon Dioxide Voluette Ampule Standard for Carbon Dioxide, 10,000 mg/L CO_2.
2. Use a TenSette Pipet (Cat. No. 19700-01) to add 0.1 mL of standard to the sample titrated in step 6. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using additions of 0.2 mL and 0.3 mL. Titrate to the same end point after each addition.
4. Each 0.1 addition of standard should require 50 additional digits of 0.3636 N titrant or five digits of 3.636 N titrant. If these uniform increases do not occur, refer to *Section 3.2.2 Standard Additions* on page *46*.

Summary of Method

Acidity due to carbon dioxide in a sample is titrated with sodium hydroxide to a phenolphthalein end point. Strong acids are assumed to be absent or of insignificant concentration. See *Appendix A, Chemical Procedures Explained*.

Required Reagents (varies with sample characteristics)

Description	Unit	Cat. No.
Carbon Dioxide Reagent Set (about 100 tests)		22727-00
Includes:		
Phenolphthalein Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 0.3636 N	each	14378-01
Sodium Hydroxide Titration Cartridge, 3.636 N	each	14380-01
Water, deionized	4 L	272-56

Required Apparatus

Digital Titrator	each	16900-01
Select one or more based on sample concentration:		
Flask, Erlenmeyer, 250-mL	each	505-46
Flask, Erlenmeyer, 125-mL	each	505-43

Required Standards

Carbon Dioxide Standard Solution, Voluette® Ampule, 10,000-mg/L as CO_2, 10-mL	16/pkg	14275-10
Phenolphthalein Indicator Solution, 5-g/L	100 mL MDB	162-32
Potassium Acid Phthalate Standard Solution, 100-mg/L as CO_2	100 mL	2261-42

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FAX: (970) 669-2932

Method 8203 Phenolphthalein and Total using Sulfuric Acid Method

Digital Titrator (10 to 4000 mg/L as $CaCO_3$)

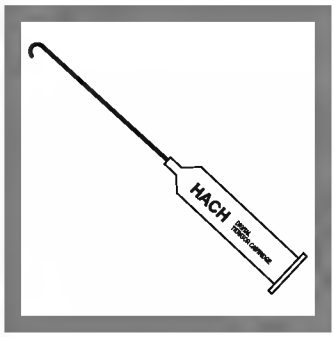
Scope and Application: For water, wastewater, and seawater

Tips and Techniques

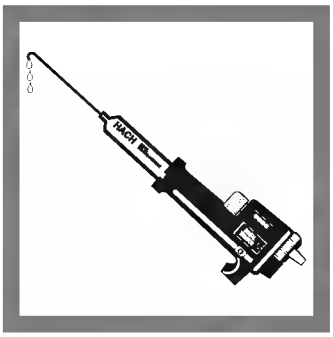
- For added convenience when stirring, use the TitraStir® apparatus (Cat. No. 19400-00, -10).
- Four drops of Phenolphthalein Indicator Solution (Cat. No. 162-32) may be substituted for the Phenolphthalein Indicator Powder Pillow.
- Four drops of Bromcresol Green-Methyl Red Indicator Solution (Cat. No. 23292-32) may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow.
- meq/L Alkalinity = mg/L as $CaCO_3$ ÷ 50

Digital Titrator Method 8203

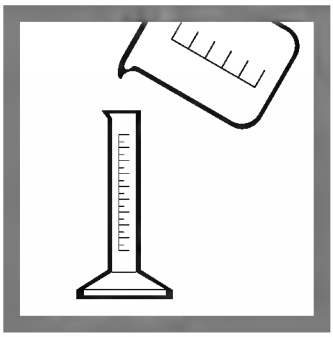
1. Select the sample volume and Sulfuric Acid (H_2SO_4) Titration Cartridge that correspond to the expected alkalinity concentration as mg/L calcium carbonate ($CaCO_3$) from *Table 1*.



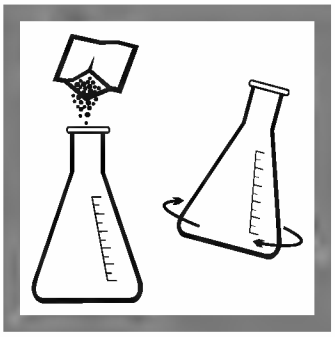
2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.



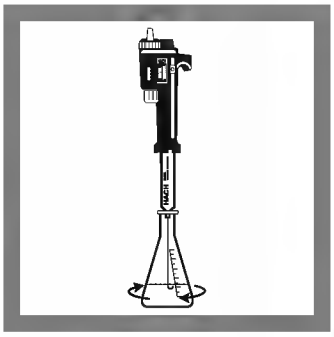
3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean, 250-mL Erlenmeyer flask. Dilute to the 100-mL mark with deionized water, if necessary.



5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.

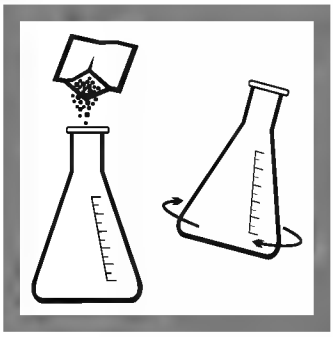


6. If the solution turns pink, titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required.

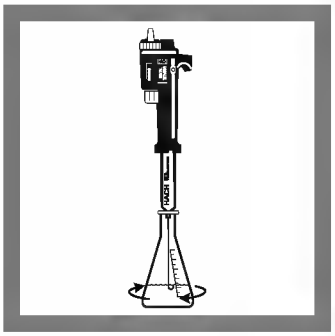
If the solution is colorless before titrating with Sulfuric acid, the Phenolphthalein (P) alkalinity is zero. Proceed to step 8.

7. Calculate:

Digits Required X
Digit Multiplier =
mg/L as $CaCO_3$ P Alkalinity



8. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the flask. Swirl to mix.



9. Continue the titration with sulfuric acid to a light pink (pH 4.5) color. as required by sample composition. Record the number of digits required.

Note: *A pH meter may be used to titrate to a specific pH as required by sample composition. See Table 2.*

10. Calculate:

Digits Required X
Digit Multiplier =
mg/L as $CaCO_3$ Total (T or M) Alkalinity

Carbonate, bicarbonate, and hydroxide concentrations may be expressed individually using the relationships shown in *Table 3*.

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (N H_2SO_4)	Catalog Number	Digit Multiplier
10–40	100	0.1600	14388-01	0.1
40–160	25	0.1600	14388-01	0.4
100–400	100	1.600	14389-01	1.0
200–800	50	1.600	14389-01	2.0
500–2000	20	1.600	14389-01	5.0
1000–4000	10	1.600	14389-01	10.0

Table 2 End Point pH

Sample Composition	End Point	Phenolphthalein Alkalinity
Alkalinity about 30 mg/L	pH 4.9	pH 8.3
Alkalinity about 150 mg/L	pH 4.6	pH 8.3
Alkalinity about 500 mg/L	pH 4.3	pH 8.3
Silicates or phosphates present	pH 4.5	pH 8.3
Industrial wastes or complex system	pH 4.5	pH 8.3
Routine or Automated Analyses	pH 4.5	pH 8.3

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before analyzing.

Alkalinity Relationship Table

Total alkalinity primarily includes hydroxide, carbonate and bicarbonate alkalinities. The concentration of these alkalinities in a sample may be determined when the phenolphthalein and total alkalinities are known (see *Table 3*).

Table 3 Alkalinity Relationship

Row	Result of Titration	Hydroxide Alkalinity Equals:	Carbonate Alkalinity Equals:	Bicarbonate Alkalinity Equals:
1	Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one-half of Total Alkalinity	0	Phenolphthalein Alkalinity times 2	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one-half of Total Alkalinity	0	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one-half of Total Alkalinity	2 times Phenolphthalein Alkalinity minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

To use the table follow these steps:

a. Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.

b. Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.

c. Divide the total alkalinity by 2 to give one-half the total alkalinity.

d. Select Row 3, 4, or 5 based on comparing the result of step c (one-half total alkalinity) with the total alkalinity.

e. Perform the required calculations in the appropriate row, if any.

f. Check your results. The sum of the three alkalinity types will equal the phenolphthalein alkalinity.

For example:

A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity. What is the concentration of hydroxide, carbonate and bicarbonate alkalinities?

The phenolphthalein alkalinity does not equal 0 (it is 170 mg/L), see step a.

The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L), see step b.

One-half of the total alkalinity (250 g/L) equals 125 mg/L. Because the phenolphthalein alkalinity (170 mg/L) is greater than one-half the total alkalinity (125 mg/L), select Row 5.

The hydroxide alkalinity is equal to:

2 x 170 = 340

340 - 250 = 90 mg/L hydroxide alkalinity

The carbonate alkalinity is equal to:

250 - 170 = 80

80 x 2 = 160 mg/L carbonate alkalinity

The bicarbonate alkalinity equals 0 mg/L.

Check: (See step f)

90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity + 0 mg/L bicarbonate alkalinity = 250 mg/L

The above answer is correct; the sum of each type equals the total alkalinity.

Accuracy Check

End Point Confirmation

A solution of one pH 8.3 Buffer Powder Pillow (Cat. No. 898-68) and one Phenolphthalein Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.

A solution of one Bromcresol Green-Methyl Red Powder Pillow and one pH 4.5 Buffer Powder Pillow (895-68) in 50 mL of deionized water is recommended as a comparison for judging the pH 4.5 end point color.

Standard Additions Method (Sample Spike)

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off an Alkalinity Voluette® Ampule Standard, 0.500 N.
2. Use a TenSette Pipet (Cat. No. 19700-01) to add 0.1 mL of standard to the sample titrated in steps 6 or 9. Resume titration back to the same end point. Record the number of digits needed.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 25 additional digits of 1.600 N titrant or 250 digits of 0.1600 N titrant. If these uniform increases do not occur, refer to *Section 3.4 Method Performance* to determine the cause.

Interferences

Highly colored or turbid samples may mask the color change at the end point. Use a pH meter (Cat. No. 51700-10) for these samples, titrating to a pH 8.3 for phenolphthalein alkalinity and the appropriate pH (see *Table 2*) for total alkalinity.

Chlorine at levels above 3.5 mg/L may cause a yellow-brown color upon the addition of the Bromcresol Green-Methyl Red Powder Pillow. Add one drop of 0.1 N Sodium Thiosulfate (Cat. No. 323-32) to eliminate this interference.

Summary of Method

The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titration to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator, and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 3.7 and 5.1, and includes all carbonate, bicarbonate and hydroxide. Alternatively, total alkalinity end points may be determined by using a pH meter and titrating to the specific pH required for the sample composition.

Alkalinity

Required Reagents

Description	Unit	Cat. No
Alkalinity Reagent Set (about 100 tests) (varies with sample characteristics)		22719-00
Includes:		
Bromcresol Green-Methyl Red Powder Pillows	100 / pkg	943-99
Phenolphthalein Powder Pillows	100 / pkg	942-99
Sulfuric Acid Titration Cartridge, 1.600 N	each	14389-01
Sulfuric Acid Titration Cartridge, 0.1600 N	each	14388-01
Water, demineralized	4 L	272-56

Required Apparatus

Select one or more based on sample concentration		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46

Required Standards

Alkalinity Standard Solution, Voluette® Ampule 0.500 N Na_2CO_3, 10-mL	16 / pkg	14278-10
Buffer Powder Pillows, pH 4.5	25 / pkg	895-68
Buffer Powder Pillows, pH 8.3	25 / pkg	898-68

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✔Method 8221

Buret Titration Method* **

Buret Titration (0 to 5,000 mg/L as $CaCO_3$)

Scope and Application: For water, wastewater, and seawater

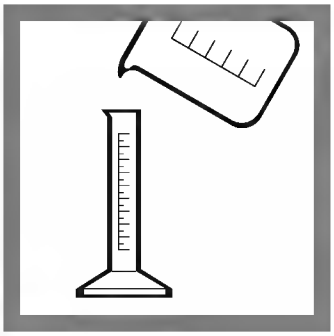
* Adapted from *Standard Method for the Examination of Water and Wastewater, 2320 B.*
** USEPA Accepted

Tips and Techniques

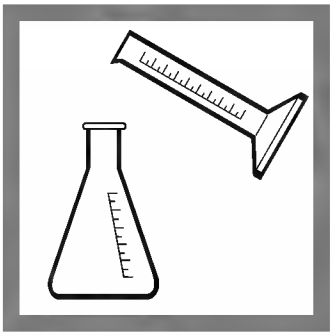
- A pH meter (Cat. No. 51700-10) is required for NPDES reporting and is recommended for best results.
- You can substitute six drops of Phenolphthalein Indicator Solution (Cat. No. 162-32) for the Phenolphthalein Indicator Powder Pillow.
- You can substitute six drops of Bromcresol Green-Methyl Red Indicator Solution (Cat. No. 23292-32) for the Bromcresol Green-Methyl Red Powder Pillow.
- mg/L as $CaCO_3$ ÷ 17.12 = grains per gallon

Buret Titration Method 8221

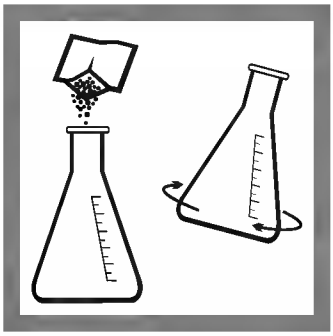
1. Select a sample size that corresponds to the expected alkalinity concentration in mg/L as calcium carbonate ($CaCO_3$) from *Table 1*.



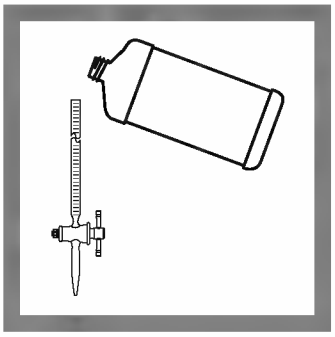
2. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*.



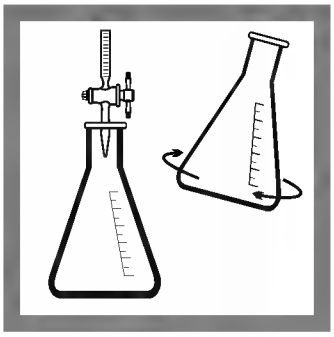
3. Transfer the sample into a 250-mL Erlenmeyer flask. If necessary, dilute to 50 mL with deionized water.



4. Add the contents of one Phenolphthalein Indicator Powder Pillow. Swirl to mix. Skip this step if you are using a pH meter.



5. Fill a 25-mL buret to the zero mark with 0.020 N Sulfuric Acid Standard Solution.



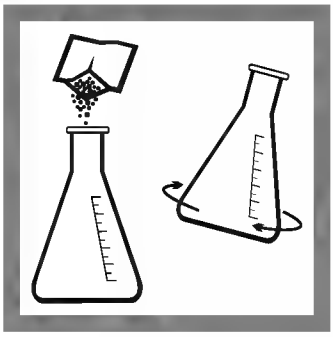
6. Titrate the sample while swirling the flask until the solution changes from pink to colorless.

When using a pH meter, the end point is 8.3.

If the solution is colorless before titrating with sulfuric acid, the phenolphthalein alkalinity is zero.

7. Calculate:

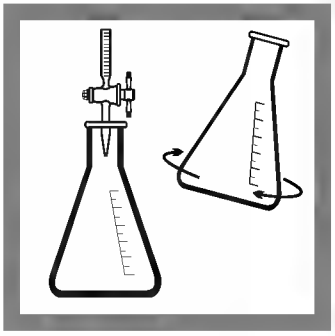
mL Titrant x Multiplier Used = mg/L Phenolphthalein Alkalinity as $CaCO_3$



8. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the titrated sample. Swirl to mix.

Do not add indicator if a pH meter is used.

Note: *Specific sample composition may require titration to a specific pH (see Table 3).*



9. Continue the titration until a light pink end point is reached.

10. Calculate:

mL Titrant x Multiplier Used = mg/L Total Alkalinity as $CaCO_3$

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (N)	Catalog Number	Multiplier
0–500	50	0.020	203-53	20
400–1000	25	0.020	203-53	40
1000–2500	10	0.020	203-53	100
2000–5000	5	0.020	203-53	200

The end points in *Table 2* are recommended for determining total alkalinity in water samples of various compositions and alkalinity concentrations.

Table 2 Alkalinity Endpoints

Sample Composition	End Point pH	
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity about 30 mg/L	pH 4.9	pH 8.3
Alkalinity about 150 mg/L	pH 4.6	pH 8.3
Alkalinity about 500 mg/L	pH 4.3	pH 8.3
Silicates or phosphates present	pH 4.5	pH 8.3
Industrial wastes or complex system	pH 4.5	pH 8.3
Routine or Automated Analyses	pH 4.5	pH 8.3

Total alkalinity primarily includes hydroxide, carbonate, and bicarbonate alkalinities. The concentration of these types in a sample may be determined when the phenolphthalein and total alkalinities are known. See *Table 3*.

Table 3 Alkalinity Relationship

Row	Result of Titration	Hydroxide Alkalinity Equals:	Carbonate Alkalinity Equals:	Bicarbonate Alkalinity Equals:
1	Phenolphthalein Alkalinity equal to 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one-half of Total Alkalinity	0	Phenolphthalein Alkalinity times 2	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one-half of Total Alkalinity	0	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one-half of Total Alkalinity	2 times Phenolphthalein Alkalinity minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

To use *Table 3*, follow these steps:

a. Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.

b. Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.

c. Divide the total alkalinity by 2 to calculate one-half the total alkalinity.

d. Select Row 3, 4 or 5 based on comparing the result of step c (one-half total alkalinity) with the phenolphthalein alkalinity.

e. Perform the required calculations if any.

f. Check your results. The sum of the three alkalinity types will equal the total alkalinity.

Example:

A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity. What is the concentration of hydroxide, carbonate, and bicarbonate alkalinities?

a. The phenolphthalein alkalinity does not equal zero but 170 mg/L.

b. The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L).

c. One-half of the total alkalinity equals 125 mg/L.

d. Because the phenolphthalein alkalinity of 170 mg/L is greater than one-half the total alkalinity of 125 mg/L, select Row 5.

The hydroxide alkalinity is equal to:

2 x 170 = 340

340 - 250 = 90 mg/L hydroxide alkalinity

The carbonate alkalinity is equal to:

250 - 170 = 80

80 x 2 = 160 mg/L carbonate alkalinity

The bicarbonate alkalinity is equal to zero mg/L.

Check:

90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity + 0 mg/L bicarbonate alkalinity = 250 mg/L

The answer is correct.

The sum of each type equals the total alkalinity (250 mg/L).

Sampling and Storage

Collect samples in plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation and prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before analyzing.

Accuracy Check

End Point Confirmation

- To accurately determine the phenolphthalein alkalinity end point, mix the contents of one Phenolphthalein Indicator Powder Pillow and the contents of one pH 8.3 Buffer Powder Pillow with 50 mL of deionized water in a 250-mL Erlenmeyer flask. The resulting color is the end point. The buffer solution without the indicator can be used to standardize a pH meter.
- To accurately determine the total alkalinity end point, mix the contents of one pH 4.5 Buffer Powder Pillow and the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow with 50 mL of deionized water in a 250-mL Erlenmeyer flask. Titrate to a light pink color change.

Standard Additions Method (Sample Spike)

Perform the standard additions method check as follows:

1. Snap the neck off an Alkalinity Voluette® Ampule Standard Solution, 0.500 N.
2. Use the TenSette Pipet (Cat. No. 19700-01) to add 0.1 mL of standard to the sample titrated in *step 6* or *step 9*. Resume titration back to the same end point. Record the volume of titrant needed.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. The mL of titrant required should increase by 2.5 mL for each 0.1 mL increment of standard added.

Interferences

Chlorine at levels above 3.5 mg / L cause a yellow-brown color upon the addition of the Bromcresol Green-Methyl Red Indicator Powder Pillow. Residual chlorine interference with the indicator may be removed by adding a drop of 0.1 N Sodium Thiosulfate Standard Solution (Cat. No. (323-32).

Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples, titrating to pH 8.3 for phenolphthalein alkalinity and the appropriate pH (see *Table 2*) for total alkalinity.

Summary of Method

Alkalinity is expressed as P (phenolphthalein) alkalinity or as T (total) alkalinity. Both types are determined by titration with a Sulfuric Acid Standard Solution to an end point evidenced by the color change of an indicator solution or determined with a pH meter. The P alkalinity is determined by titration to a pH of 8.3 and registers the total hydroxide and one half the carbonate present. The T alkalinity is determined by titration to a pH of 4.5. The total alkalinity includes all carbonate, bicarbonate and hydroxide alkalinity. Alternatively, total alkalinity end points may be determined by using a pH meter and titrating to the specific pH required for the sample composition.

Alkalinity

Required Reagents

Description	Quantity Required Per Test	Unit	Cat. No.
Bromcresol Green-Methyl Red Indicator Powder Pillows	1 pillow	100 / pkg	943-99
Phenolphthalein Indicator Powder Pillows	1 pillow	100 / pkg	942-99
Sulfuric Acid Standard Solution, 0.020 N	varies	1 L	203-53

Required Apparatus

Buret Clamp, double	1	each	328-00
Buret, Class A, 25-mL	1	each	26365-40
Select one or more based on sample volume:			
Cylinder, graduated, 5-mL		each	508-37
Cylinder, graduated, 10-mL		each	508-38
Cylinder, graduated, 25-mL		each	508-40
Cylinder, graduated, 50-mL		each	508-41
Flask, Erlenmeyer, 250-mL	1	each	505-46
Funnel, Micro	1	each	25843-35
Support Stand	1	each	563-00

Required Standards

Alkalinity Standard Solution, Voluette® Ampules, 0.500 N, 10-mL	16 / pkg		14278-10
Buffer Powder Pillows, pH 4.5	25		895-68
Buffer Powder Pillows, pH 8.3	25		898-68
Water, deionized	4 L		272-56

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

16900-08

Digital Titrator

Model 16900

al/cth 8/97 23 ed
jnb/dk rev 4, 12/00

TRADEMARKS OF HACH COMPANY

AccuGrow®
AccuVac®
AccuVer™
AccuVial™
Add-A-Test™
AgriTrak™
AluVer®
AmVer™
APA 6000™
AquaChek™
AquaTrend®
BariVer®
BODTrak™
BoroTrace™
BoroVer®
C. Moore Green™
CA 610™
CalVer®
ChromaVer®
ColorQuik®
CoolTrak®
CuVer®
CyaniVer®
Digesdahl®
DithiVer®
Dr. F. Fluent™
Dr. H. Tueau™
DR/Check™
EC 310™
FerroMo®
FerroVer®
FerroZine®
FilterTrak™ 660
Formula 2533™
Formula 2589™
Gelex®
H_2O University™
H_2OU™
Hach Logo®
Hach One®
Hach Oval®
Hach.com™
HachLink™
Hawkeye The Hach Guy™
HexaVer®
HgEx™
HydraVer®
ICE-PIC™
IncuTrol®
Just Add Water™
LeadTrak®
M-ColiBlue24®
ManVer®
MolyVer®
Mug-O-Meter®
NetSketcher™
NitraVer®
NitriVer®
NTrak®
OASIS™
On Site Analysis.
Results You Can Trust℠
OptiQuant™
OriFlow™
OxyVer™
PathoScreen™
PbEx®
PermaChem®
PhosVer®
Pocket Colorimeter™
Pocket Pal™
Pocket Turbidimeter™
Pond In Pillow™
PourRite®
PrepTab™
ProNetic™
Pump Colorimeter™
QuanTab®
Rapid Liquid™
RapidSilver™
Ratio™
RoVer®
*sens**ion***™
Simply Accurate℠
SINGLET™
SofChek™
SoilSYS™
SP 510™
Spec√™
StablCal®
StannaVer®
SteriChek™
StillVer®
SulfaVer®
Surface Scatter®
TanniVer®
TenSette®
Test 'N Tube™
TestYES!℠
TitraStir®
TitraVer®
ToxTrak™
UniVer®
VIScreen™
Voluette®
WasteAway™
ZincoVer®

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SPECIFICATIONS

Digital Titrator

Delivery: 800 digits/mL or 0.00125 mL/digit

Accuracy*: ± 1% for readings over 100 digits. (Uncertainty of readings is 1 digit. Most samples require more than 100 digits.)

Weight: 132 g (4.7 oz.)

Cartridges for the Digital Titrator

Volume: 13 mL

Number of tests: Most reagents are formulated to provide 100 typical titrations; the number may vary depending on sample concentration.

Weight (full): 56.75 g (2 oz.)

* Overall method accuracy includes, in addition to the Digital Titrator, other sources of error controlled by the analyst. The other sources of error include: sampling, sample volume, dilution (if required), end point detection, reagent quality, and interferences.

OPERATION

DANGER

Handling chemical samples, standards, and reagents can be dangerous. Review the necessary Material Safety Data Sheets and become familiar with all safety procedures before handling any chemicals.

DANGER

La manipulation des échantillons chimiques, étalons et réactifs peut être dangereuse. Lire les Fiches de Données de Sécurité des Produits (FDSP) et se familiariser avec toutes les procédures de sécurité avant de manipuler tous les produits chimiques.

PELIGRO

La manipulación de muestras químicas, estándares y reactivos puede ser peligrosa. Revise las fichas de seguridad de materiales y familiarícese con los procedimientos de seguridad antes de manipular productos químicos.

GEFAHR

Das Arbeiten mit chemischen Proben, Standards und Reagenzien ist mit Gefahren verbunden. Es wird dem Benutzer dieser Produkte empfohlen, sich vor der Arbeit mit sicheren Verfahrensweisen und dem richtigen Gebrauch der Chemikalien vertraut zu machen und alle entsprechenden Materialsicherheitsdatenblätter aufmerksam zu lesen.

PERIGO

A manipulação de amostras, padrões e reagentes químicos pode ser perigosa. Reveja a folha dos dados de segurança do material e familiarize-se com todos os procedimentos de segurança antes de manipular quaisquer produtos químicos.

GENERAL DESCRIPTION

1.1 Introduction

Hach's Digital Titrator is a new concept in titrimetric analysis. It is a precision dispensing device fitted with compact cartridges that contain concentrated titrants. Accurate titrations are made without the bulk and fragility of conventional burets.

A main drive screw in the Digital Titrator controls a plunger which forces the concentrated titrant from a titration cartridge in a carefully regulated flow. The titrator body is constructed of precision-molded, heavy-duty, chemical- and impact-resistant acetal plastic. Accuracy is rated at ± 1% or better for a titration of more than 100 digits. For titrations less than 100, accuracy is ± 1 digit.

Titration solutions (titrants) are packaged in disposable polypropylene or Kynar® containers with Teflon-covered neoprene seals and polyethylene resealable closures to cover the cartridge tips. Each cartridge contains approximately 13 mL of titrating solution, enough for 50–100 average titrations. Titrant solutions are typically controlled to ± 0.5% concentration with normality and tolerances listed on the label. Titrant concentrations are designed for titrations of 10 to 40 turns (100 to 400 digits) of the delivery knob. For the most commonly used concentration ranges, the digits appearing in the counter window correspond to the sample concentration.

Figure 1 Hach Digital Titrator

Both portable and fixed-position titrations are possible with the Digital Titrator. The instrument has a grip for hand-held operation or it can be clamped to a TitraStir® Stir Plate or laboratory stand for stationary setups. See *Figure 1*.

Each Digital Titrator comes with five delivery tubes and a methods manual, which covers the most commonly tested parameters and the corresponding titrant cartridges. Right-angle (ninety-degree) delivery tubes for stationary setups are available as an optional accessory.

1.1.1 Following a Procedure for the First Time

Each method is divided into five sections: Procedure, Accuracy Check, Interferences, Summary of Method, and Reagents and Apparatus. For more information about how to select a procedure or for answers to chemical questions, see Hach's *Water Analysis Handbook* (literature 8376). For more information about chlorine measurement, also see the technical booklet titled, *Current Technology of Chlorine Analysis for Water and Wastewater* (literature 7019).

The **Procedure** details how to perform the method step-by-step. To select the appropriate sample volume and titration cartridge based on expected sample concentration, use the tables provided in each procedure. If the expected sample concentration is not known, start with one of the smaller sample volumes and determine its approximate concentration. Retest with the appropriate sample size.

The ranges in the table overlap to offer more flexibility. In most procedures, the number of digits used for each concentration range will be 100 to 400 digits.

To determine the actual concentration of the sample, use the correct digit multiplier for the sample volume and titration cartridge used.

Throughout the procedure, the notes will provide additional information.

The **Accuracy Check** provides a way to verify the results and determine if interferences are present. It also provides a method for checking the performance of reagents, the Digital Titrator and the operator's technique. Further information is provided in *Appendix A, Accuracy Check and Standard Additions*.

The **Interferences** section identifies common interferences causing inaccurate results and describes how to eliminate their effects. The interference levels are based on the sample volume that has 1.0 as the digit multiplier. Higher interference levels may be tolerated if a smaller sample is used.

The **Summary of Method** section discusses the chemical reaction taking place and information that applies to the entire procedure.

The **Reagents and Apparatus** list concludes the procedure. All the items required to perform the test are listed first and are available from Hach. The items listed in the notes or interferences sections are included in the optional listings.

1.2 Step-By-Step

1. Select a sample volume and titration cartridge corresponding to the expected sample concentration from the table given in each procedure.

   If the expected sample concentration is not known, start with one of the smaller sample volumes and determine its approximate concentration. Retest with the appropriate sample size.

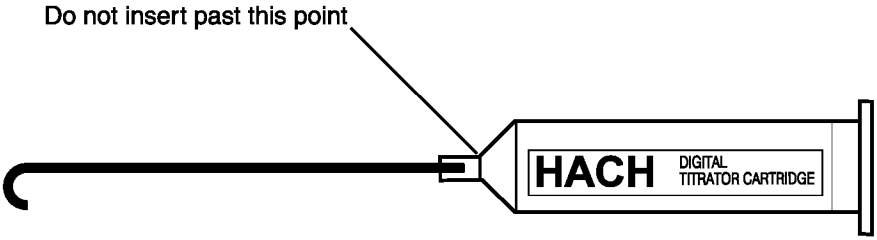
2. Slide the cartridge into the titrator receptacle and lock in position with a slight turn. See *Figure 2*.

Figure 2 Sliding the Cartridge into Place

3. Remove the polyethylene cap and insert a clean delivery tube into the end of the cartridge until it is tight. See *Figure 3*. Use a straight tube with a hook at the end for hand-held titrations; use a 90° tube with a hook at the end for stationary setups.

Do not insert tube past cartridge extension; see illustration below. In some instances, it might be necessary to remove a small burr on the leading edge of the tube before insertion.

Figure 3 Inserting the Delivery Tube



4. For stationary titrations, use a TitraStir Stir Plate or a clamp holder and clamp to attach the titrator to a laboratory stand. See *Figure 4* and *Figure 5*.

The TitraStir Stir Plate holds the Digital Titrator during the titration and also stirs the sample at a constant speed, leaving the analyst free to detect the end point. When a TitraStir Stir Plate is used, substitute or add the following Optional Apparatus.

APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	1	5/pkg	41578-00
Flask, Erlenmeyer, 125 mL	1	each	505-43
Flask, Erlenmeyer, 250 mL	1	each	505-46
Stir Bar, 28.6 x 7.9 mm	1	each	20953-52
TitraStir® Stir Plate, 115 Vac	1	each	19400-00
TitraStir® Stir Plate, 230 Vac	1	each	19400-10

5. To start titrant flowing and flush the delivery tube, hold the tip of the cartridge up. Advance the plunger release button to engage the piston with the cartridge (push the button in and toward the cartridge). Do not expel solution when pushing the piston toward the cartridge. Turn the delivery knob until air is expelled and several drops of solution flow from the tip. As you turn the knob a drive screw pushes a piston against the cartridge seal and forces liquid out through the delivery tube. Then use the counter reset knob to turn the digital counter back to zero and wipe the tip. The tip can be rinsed with deionized water rather than wiped, if desired.

Figure 4 Using the TitraStir® Stir Plate

Figure 5 Using a Laboratory Stand

Figure 6 Titrating the Sample

6. Use the smallest appropriate graduated cylinder or pipet to measure the sample volume from the given table. Transfer the sample into a 125-mL or 250-mL Erlenmeyer flask. Dilute to the appropriate total volume with deionized water if necessary.

Note: *Sample volume measurements and dilutions (if required) must be made accurately. However, final total volume of titrated solution is not critical.*

7. Add the necessary reagents to the sample and swirl to mix.

8. Immerse the delivery tube tip in the solution and swirl the flask while titrating. Titrate by turning the delivery knob. Keep turning the knob and swirling the sample until the end point is reached. Record the number of digits that appear in the digital counter window. See *Figure 6*.

Note: *The number of digits required will usually range from 100 to 400. In nearly all of the procedures if the digits required is less than 100 or more than 400, an alternate sample volume or titrant cartridge should be used.*

Note: *Inaccurate results will occur if the delivery tube tip is held out of the solution rather than under the solution surface.*

9. Calculate the concentration of your sample by using the following formula:

Digits Required × Digit Multiplier = Sample Concentration

Where:

Digits Required = the number that appeared in the digital counter window in Step 8.

Digit Multiplier = the number from the table given in the procedure. It takes into account the sample dilution and titrant strength.

10. After completing testing for the day, press the plunger release button and manually retract the plunger into the body of the titrator. Remove the cartridge. Remove the delivery tube and reseal the cartridge with the polyethylene cap. See *Figure 7*.

Figure 7 Retracting the Plunger

11. Discard or clean the delivery tube immediately after use. To clean, force water, then air, into the tube opening with a syringe or wash bottle.

1.3 Helpful Hints

1.3.1 To Reuse a Partially Emptied Cartridge

1. With the plunger fully retracted, attach cartridge to the titrator.
2. Press the plunger release; then manually push the plunger against the cartridge seal.
3. Attach a delivery tube. Hold the tip of the cartridge up. Eject air and a few drops of titrant, zero the counter, and wipe the tip.
4. Titrate as usual.

1.3.2 To Calculate Titrant Volume Used

Normalities of many Hach titration cartridge solutions have been designed so that the number of digits used in a titration corresponds to the sample concentration in mg/L. To determine the volume used in mL, divide the Digital Titrator reading by 800.

1.3.3 To Fill Your Own Titration Cartridges

Cartridges may be cleaned and refilled, or new empty cartridges, Cat. No. 14495-01, can be purchased from Hach Company. See *Figure 8*. When preparing to refill old cartridges, push the cartridge seal out of the cartridge with air pressure applied through the tip. Cap the tip, fill with solution and reinsert the cartridge seal using care to avoid wrinkling the Teflon sheath. Filling also can be accomplished at the tip with a syringe.

Figure 8 Digital Titrator Cartridges

1.3.4 Verifying Technique

Whenever procedures are changed or new equipment is used, it is helpful to run a sample of known concentration. This technique will confirm the operator is following the procedure correctly and the new equipment is working properly. One objective important to Hach Company is making our tests self-verifying. This means Hach makes the tools available so the operator can check their own work for accurate results without relying on an outside lab or chemist.

For most of the tests in this manual, *Table 1* on page *20* lists each procedure, the suggested standard, the volume of standard needed, the titration cartridge used, and the number of expected digits when the test is performed correctly. The suggested standards are Voluette® or PourRite™ Ampules whenever possible because of their superior accuracy and stability.

To use titration standards follow these steps:

1. Select the procedure of interest and order the appropriate standard. Use the given catalog numbers.
2. Measure the volume of standard to be used as the sample in the procedure using a TenSette® Pipet or Class A pipet.
3. Perform the procedure as written, adding deionized water as necessary.
4. After titrating, the required number of digits should approximately equal the expected digits.

Call Hach Technical and Customer Service (1-800-227-4224) for additional help.

.

Table 1 Titration Standards

Procedure (Parameter)	Standard Description (Cat. No.)	Volume of Standard (mL)	Titration Cartridge (Cat. No.)	Expected Digits
Acid-Base: Acid	0.500 N H_2SO_4 (2121-26)	1.0	1.600 N NaOH (14379-01)	250
		5.0	8.00 N NaOH (14381-01)	250
Base	0.500 N Na_2CO_3 (14278-10)	1.0	1.600 N H_2SO_4 (14389-01)	250
		5.0	8.00 N H_2SO_4 (14391-01)	250
Acidity	0.500 N H_2SO_4 (2121-26)	0.1	0.1600 N NaOH (14377-01)	250
		1.0	1.600 N NaOH (14379-01)	250
Alkalinity	0.500 N Na_2CO_3 (14278-10)	0.1	0.1600 N H_2SO_4 (14388-01)	250
		1.0	1.600 N H_2SO_4 (14389-01)	250
Calcium*: mg/L $CaCO_3$	10,000 mg/L $CaCO_3$ (2187-10)	0.1	0.0800 M EDTA (14364-01)	100
		1.0	0.800 M EDTA (14399-01)	100
G.d.h.	10,000 mg/L $CaCO_3$ (2187-10)	0.2	0.1428 M EDTA (14960-01)	112
		1.0	0.714 M EDTA (14959-01)	112
Carbon Dioxide	10,000 mg/L CO_2 (14275-10)	0.2	0.3636 N NaOH (14378-01)	100
		2.0	3.636 N NaOH (14380-01)	
Chloride	12,500 mg/L Cl (14250-10)	0.1	0.2256 N $Hg(NO_3)_2$ (14393-01)	125
		0.1	0.2256 N $AgNO_3$ (14396-01)	125
		1.0	1.128 N $AgNO_3$ (14397-01)	250
		1.0	2.256 N $Hg(NO_3)_2$ (921-01)	125

Table 1 Titration Standards (Continued)

Procedure (Parameter)	Standard Description (Cat. No.)	Volume of Standard (mL)	Titration Cartridge (Cat. No.)	Expected Digits
Chlorine	~50 mg/L Cl_2 (14268-20) (see certificate)	2.0	0.02256 N $Na_2S_2O_3$ (24091-01)	varies**
	~25 mg/L Cl_2 (26300-20)	0.5	0.00564 N FEAS (22923-01)	varies***
Chromate	1000 mg/L Cr (2231 mg/L CrO_4) (14664-42)	1.0	0.2068 N $Na_2S_2O_3$ (22676-01)	223
Hardness: mg/L $CaCO_3$	10,000 mg/L $CaCO_3$ (2187-10)	0.1	0.0800 M EDTA (14364-01)	100
		0.1	0.0800 M CDTA (14402-01)	100
		1.0	0.800 M EDTA (14399-01)	100
		1.0	0.800 M CDTA (14403-01)	100
G.d.h.	10,000 mg/L $CaCO_3$ (2187-10)	0.2	0.1428 M EDTA (14960-01)	112
		1.0	0.714 M EDTA (14959-01)	112
Iron	50 mg/L Fe (14254-10)	10.0	0.0716 M TitraVer (20817-01)	200
	1000 mg/L Fe (2271-42)	10.0	0.716 M TitraVer (20818-01)	100
Oxygen, Dissolved****	10 mg/L as DO (401-11)	100	0.2000 N $Na_2S_2O_3$ (22675-01)	500
		200	2.00 N $Na_2S_2O_3$ (14401-01)	100
Sulfite	5000 mg/L SO_3 (22674-10)	1.0	0.3998 N KIO_3–KI (14961-01)	250

* One to two drops of Magnesium Standard Solution (10 g/L as $CaCO_3$) must be added to get a sharp end point. These added drops will not change the results.

** The expected digits equal the volume of standard times the concentration on the certificate (e.g., 2 mL x 50 mg/L = 100 digits).

*** The expected digits equals the volume of standard times the concentration on the certificate times the constant, 4. (Example: 0.5 mL x 50 mg/L x 4 = 100 digits)

**** Add one Sulfamic Acid Powder Pillow to the volume of standard and follow Steps 10 to 12 in the Dissolved Oxygen Procedure. It is not necessary to add the first two reagents.

1.4 Adapting a Buret Titration to the Digital Titrator

Adapt any standard titration procedure using a buret to the Digital Titrator by using the following procedure.

1. Determine the approximate number of digits required. The Digital Titrator dispenses 1 mL per 800 digits on the counter. Using the following equation, determine the digits required for your buret method.

$$\text{Digits Required} = \frac{N_t \times mL_t \times 800}{N_c}$$

Where:

N_t = Normality of buret titrant
mL_t = milliliters of buret titrant required for an average titration
N_c = Normality of Digital Titrator cartridge

2. If the number of digits required is within the range of 70 to 350, you can use the procedure as written, substituting the Digital Titrator directly for the buret. Or, if the number of digits is outside of this range, make the following modifications:

a. If the number of digits required is more than 350, reduce the sample size to save titrant.

b. If the number of digits required is less than 70, increase the sample size to increase precision.

c. If the sample size is altered, adjust the amount of buffering or indicating reagents by the same proportion.

3. When using the Digital Titrator for your buret method, note the number of digits required for a sample titration. To convert the digits required to the equivalent number of milliliters if the buret method was used, calculate:

$$\text{Equivalent Buret Milliliters} = \text{Digits Required} \times \frac{N_c}{800 \times N_t}$$

If the sample size was changed, adjust the equivalent buret milliliters accordingly. If the sample size was increased, reduce the equivalent buret milliliters; if the sample size was reduced increase the equivalent buret milliliters. Multiply the equivalent

buret milliliters by any normally used factors to calculate concentration in oz/gal, g/L, etc.

Example: Adapt a buret procedure, which normally requires about 20 mL of a 0.4 N titrant, to the Digital Titrator. Try an 8.0 N titration cartridge. The first equation above gives:

$$\text{Digits Required} = \frac{0.4 \times 20 \times 800}{8.0} = 800 \text{ digits}$$

Because this would use excessive titrant, reduce the sample size to one fourth its normal size to reduce the digits required to 200, well within the recommended range.

Upon completion of the titration using the smaller sample size, calculate the equivalent buret milliliters by the second equation above. If 205 were the digits required:

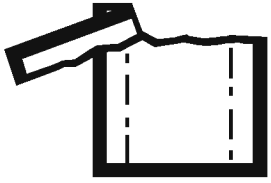
$$\text{Equivalent Buret Milliliters} = \frac{205 \times 8.0}{800 \times 0.4} = 5.13 \text{ mL}$$

Multiply the 5.13 mL by 4 to account for the reduction in sample size to give the true equivalent buret milliliters of 20.5 mL. If the buret method called for multiplying the number of milliliters of titrant by a factor to calculate the concentration of a sample component, then multiply 20.5 by that factor.

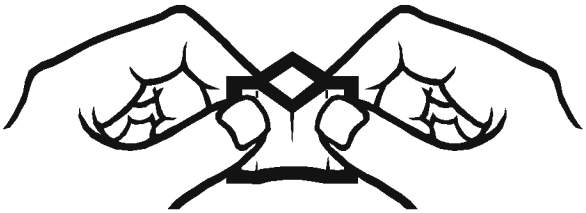
1.5 Using PermaChem® Powder Pillows

1. **Tap** the PermaChem on a hard surface to collect the powdered reagent in the bottom.

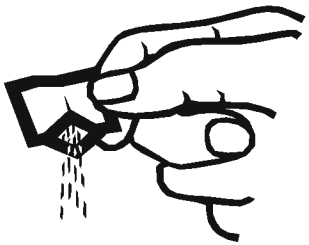
2. **Tear** across on the dotted pillow line marked “TEAR” holding the pillow away from your face.



3. Using two hands, **Push** both sides toward each other until thumbs and forefingers form a diamond. Make sure to **Crease** the foil pack, so that it forms a spout.



4. **Pour** the pillow contents into the sample. The polyfilm lining is specially formulated to deliver all the powder necessary for accurate results (no tapping on the vessel edge is necessary).



1.6 Safety

Safety is the responsibility of each individual when performing analysis procedures, and the analyst must develop and maintain good safety habits. Because many of the procedures in this methods handbook use potentially hazardous chemicals and apparatus, it is important that the analyst practice good laboratory techniques to minimize accidents. The following paragraphs present several techniques applicable to water analysis in the laboratory and in the field. They are not all inclusive, of course, nor do they apply only to the procedures provided in this handbook. They are general in nature but emphasize practices that are often key factors in personal injury incidents.

- Read labels carefully. Never remove the label from a reagent container. When preparing a reagent or standard solution, be sure to label the container clearly and date it.

- A Material Safety Data Sheet (MSDS) comes with each reagent. This sheet contains helpful information on first aid,

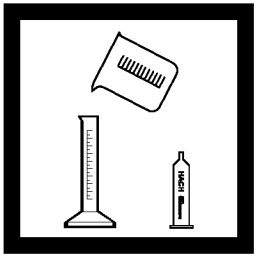
spill and disposal procedures, and precautionary measures and should be read before using the product.

- Warning labels also appear on some of the apparatus used with the test procedures.
- Wear protective clothing when handling chemicals that cause irritation or burns. Eye protection in particular is important to guard against spattering and splashes from accidental spills when caustic materials are being used.
- Use tongs or finger cots when transferring apparatus that is hot.
- Use mechanical pipetters: Mouth pipetting could result in accidentally ingesting dangerous chemicals. Make a habit of using mechanical pipet fillers for all pipetting. This will avoid mistakes that could cause serious injury.
- Use special care with dangerous chemicals and apparatus.
- Follow the test procedure steps carefully and observe all precautionary measures. It is good practice to read the entire procedure carefully before beginning the procedure. Use safety equipment, such as pipet fillers, protective clothing, and ventilating hoods, appropriate for the test being conducted. Wipe up all spills promptly. Do not smoke or eat in an area where toxic or irritating chemicals are used. Use reagents and apparatus only as they were meant to be used and use them only as directed in the test procedure. Do not use damaged labware and malfunctioning equipment.

TITRATION PROCEDURES

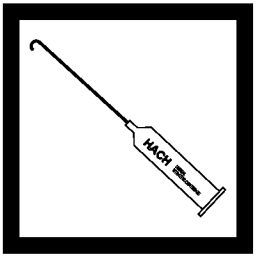
ACID-BASE (10 to 4000 mg/L as meq/L)

Acid Determination

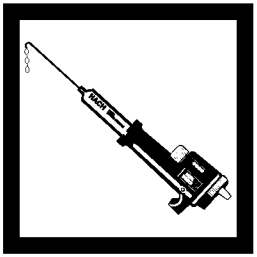


1. Select the sample volume corresponding to the expected acid concentration in milliequivalents (meq)/L or normality (N) from *Table 1*.

Note: *See Sampling and Storage following these steps.*

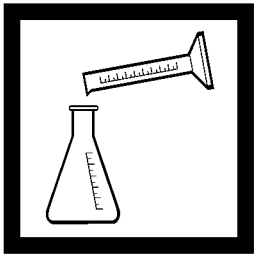


2. Insert a clean delivery tube into the appropriate Sodium Hydroxide Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step*, for assembly instructions.



3. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

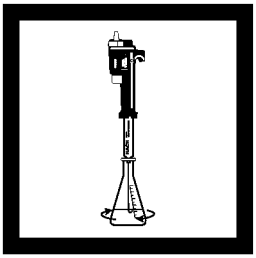
Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



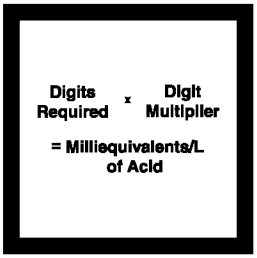
4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix. The solution should be colorless.

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*



6. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium hydroxide until a light pink color forms and persists for 30 seconds. Record the number of digits required.



7. Calculate:

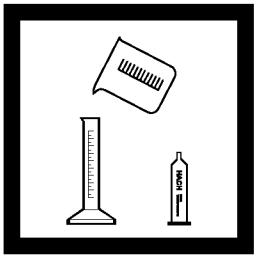
Digits Required x Digits Multiplier = Milliequivalents per Liter of Acid

Note: *To determine the normality of the sample, divide the milliequivalents per liter obtained by 1000.*

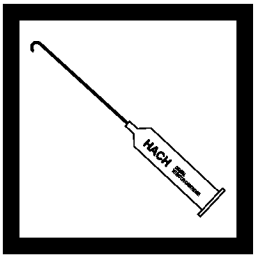
Table 1

Range meq/L	Range N	Sample Volume (mL)	Titration Cartridge	Catalog Number	Digit Multiplier
1-4	0.001-0.004	100	1.6 N NaOH 1.6 N H_2SO_4	14379-01 14389-01	0.02
4-10	0.004-0.01	50	1.6 N NaOH 1.6 N H_2SO_4	14379-01 14389-01	0.04
10-40	0.01-0.04	100	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	0.1
20-80	0.02-0.08	50	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	0.2
50-200	0.05-0.2	20	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	0.5
100-400	0.1-0.4	10	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	1.0
200-800	0.2-0.8	5	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	2.0
500-2000	0.5-2	2	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	5.0
1000-4000	1-4	1	8 N NaOH 8 N H_2SO_4 8 N HCl	14381-01 14391-01 14390-01	10.0

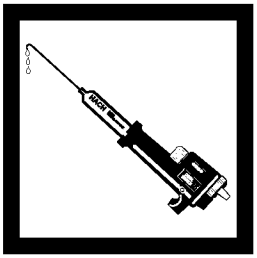
Base Determination



1. Select the sample volume corresponding to the expected base concentration in milliequivalents/L or normality from *Table 1*.

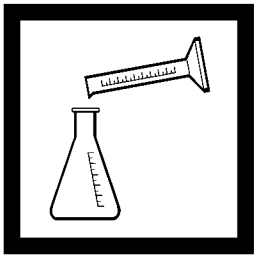


2. Insert a clean delivery tube into the appropriate Hydrochloric Acid or Sulfuric Acid Titration Cartridge. Attach the cartridge to the titrator body. See *General Description Section, Step-by-Step*, for assembly instructions, if necessary.



3. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

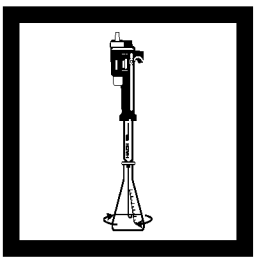
Note: *For added convenience use the TitraStir Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix. The solution should be a pink color.

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*



6. Titrate with 8.00 N hydrochloric acid or sulfuric acid until the solution is colorless. Record the number of digits required.

7. Calculate:

Digits Required x Digit Multiplier = Milliequivalents per Liter of Base

Note: *To determine the normality of the sample, divide the milliequivalents per liter obtained by 1000.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Minimize agitation or prolonged exposure to air. Sample may be stored at least 24 hours by cooling to 4 °C (39 °F) or below if they cannot be analyzed immediately. Warm to room temperature before analyzing.

Accuracy Check

Using a clean Class A 20.00 mL pipet, transfer 20.00 mL 0.100 N NaOH Standard Solution (for base determination) or 20.00 mL 0.100 N Sulfuric Acid Standard Solution (for acid determination) to a clean 250-mL Erlenmeyer flask. Dilute to about 100 mL with deionized water.

Follow the procedure for base determination using 8.00 N HCl or H_2SO_4 Titration Cartridge or for acid determination using 8.00 N NaOH Titration Cartridge. About 200 digits of titrant should be required.

Interferences

Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples.

Summary of Method

A measured amount of sample is treated with a colorimetric indicator and then titrated with a strong acid or base. The amount of titrant used is directly proportional to the milliequivalents of acid or base in the sample. These titrations also can be performed using a pH meter instead of a colorimetric indicator. In this case, titrate to pH 7 or to the pH required.

REQUIRED REAGENTS

(varies with sample characteristics)

Description	Cat. No.
Acid Determination Reagent Set (about 100 tests)	
1-10 meq/L includes: (1) 942-99, (1) 14379-01	24459-00
10-4,000 meq/L includes: (1) 942-99, (1) 14381-01	24460-00

REQUIRED REAGENTS, continued

Description	Unit	Cat. No.
Hydrochloric Acid Titration Cartridge, 8.00 N	each	14390-01
Phenolphthalein Indicator Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 1.600 N	each	14379-01
Sodium Hydroxide Titration Cartridge, 8.00 N	each	14381-01
Sulfuric Acid Titration Cartridge, 1.600 N	each	14389-01
Sulfuric Acid Titration Cartridge, 8.00 N	each	14391-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 5-mL	each	508-37
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Phenolphthalein Indicator Solution, 5 g/L	100 mL*	162-32
Sodium Hydroxide Standard Solution, 0.100 N	1000 mL	191-53
Sulfuric Acid Standard Solution, 0.100 N	1000 mL*	202-53

OPTIONAL APPARATUS

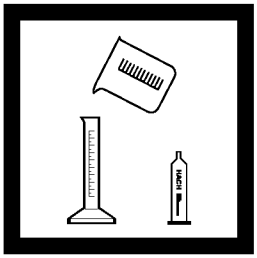
Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong, extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, volumetric, Class A, 1-mL	each	14515-35
Pipet, volumetric, Class A, 2-mL	each	14515-36
Pipet, volumetric, Class A, 5-mL	each	14515-37
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

* Contact Hach for larger sizes.

ACIDITY (10 to 4000 mg/L as $CaCO_3$)

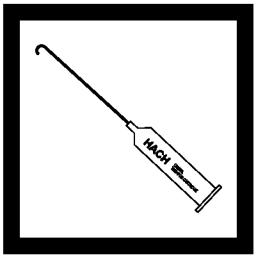
Methyl Orange and Phenolphthalein (Total) Methods

Methyl Orange Method — Method 8201

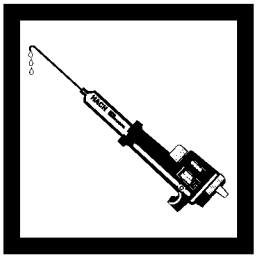


1. Select a sample volume and a Sodium Hydroxide (NaOH) Titration Cartridge corresponding to the expected acidity concentration as mg/L calcium carbonate ($CaCO_3$) from *Table 1*.

Note: *See Sampling and Storage following these steps.*

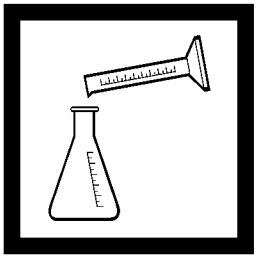


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

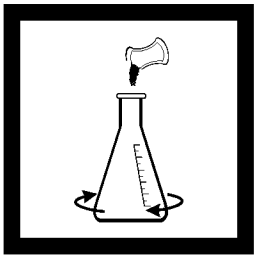


4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

Note: *Minimize agitation because dissolved gases in the sample such as carbon dioxide, hydrogen sulfide and ammonia may be lost and cause inaccurate results.*

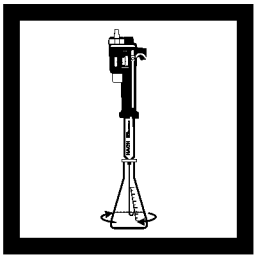
Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (N NaOH)	Catalog Number	Digit Multiplier
10-40	100	0.1600	14377-01	0.1
40-160	25	0.1600	14377-01	0.4
100-400	100	1.600	14379-01	1.0
200-800	50	1.600	14379-01	2.0
500-2000	20	1.600	14379-01	5.0
1000-4000	10	1.600	14379-01	10.0



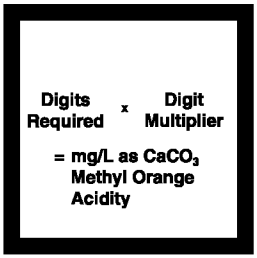
5. Add the contents of one Bromphenol Blue Indicator Powder Pillow and swirl to mix.

Note: *Six drops of Bromphenol Blue Indicator Solution may be substituted in this step.*



6. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium hydroxide from yellow to blue-violet (pH 3.7). Record the number of digits required.

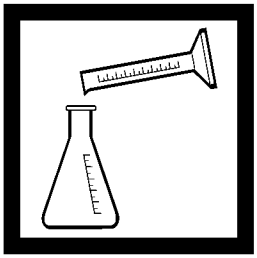
Note: *A solution of one pH 3.7 Buffer Powder Pillow and one Bromphenol Blue Indicator Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.*



7. Calculate:

Digits Required x Digit Multiplier = mg/L as $CaCO_3$ Methyl Orange Acidity

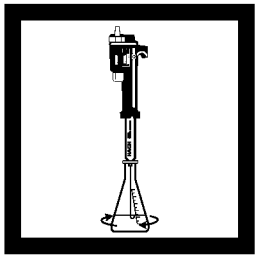
Phenolphthalein (Total) Method **Method 8202**



1. Measure a second portion of the sample selected from *step 1 on page 35* into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

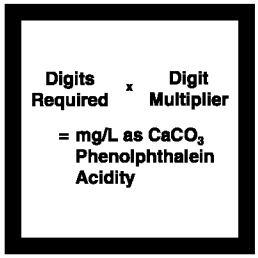
2. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*



3. Titrate with sodium hydroxide from colorless to a light pink color that persists for 30 seconds. Record the number of digits required.

Note: *A solution of one pH 8.3 Buffer Powder Pillow and one Phenolphthalein Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.*



4. Calculate:

Digits Required x Digit Multiplier = mg/L as $CaCO_3$ Phenolphthalein Acidity

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Minimize agitation or prolonged exposure to air. Samples may be stored at least 24 hours by cooling to 4 °C (39 °F) or below if they cannot be analyzed immediately. Warm to room temperature before analyzing.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off an Acidity Voluette® Ampule Standard, 0.500 N.

2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in *step 6* for methyl orange acidity or *step 3* for phenolphthalein acidity. Resume titration back to the same end point. Note the number of digits required.

3. Repeat using two more additions of 0.1 mL. Titrate to the end point after each addition.

4. Each 0.1 mL addition of standard should require 25 additional digits of 1.600 N titrant or 250 digits of 0.1600 N titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples.
- Chlorine may interfere with the indicators. Add one drop of 0.1 N Sodium Thiosulfate to eliminate this effect.
- To determine the phenolphthalein acidity of samples containing hydrolyzable metals such as iron, manganese or aluminum, use the following procedure:

  a. Adjust the sample in *step 1* for phenolphthalein acidity to pH 4.0 or less (if necessary) by using the Digital Titrator with an acid titration cartridge of identical normality to the Sodium Hydroxide Titration Cartridge used. Record the number of digits of acid added to lower the pH.

  b. Add five drops of 30% Hydrogen Peroxide Solution and boil the solution for 2-5 minutes.

  c. Cool to room temperature. Titrate following the Phenolphthalein Procedure *steps 2* and *3*. Subtract the number of digits of acid added to lower the pH from the number of digits required in *step 3* of the Phenolphthalein Procedure. Continue with *step 4*.

Summary of Method

Bromphenol blue (pH 3.7) or phenolphthalein (pH 8.3) indicator is used to titrate the sample with sodium hydroxide to a

colorimetric end point. Bromphenol blue gives a better end point than methyl orange indicator. Titration to pH 3.7 determines strong mineral acidity (also referred to as methyl orange acidity), whereas the pH 8.3 phenolphthalein end point includes weaker acid species as well, and represents the total acidity. The results are expressed in mg/L as calcium carbonate ($CaCO_3$) at a specified pH.

REQUIRED REAGENTS
(varies with sample characteristics)

Description	Unit	Cat. No.
Acidity Reagent Set (about 100 tests)		22728-00
Includes: (1) 942-99, (1) 14377-01, (1) 14379-01, (1) 14550-99		
Bromphenol Blue Powder Pillows	100/pkg	14550-99
Phenolphthalein Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 0.1600 N	each	14377-01
Sodium Hydroxide Titration Cartridge, 1.600	each	14379-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated 25-mL	each	508-40
Cylinder, graduated 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Acidity Standard Solution, Voluette® Ampules, 0.500 N H_2SO_4, 10 mL	16/pkg	14330-10
Bromphenol Blue Indicator Solution	100 mL MDB	14552-32
Buffer Powder Pillows, pH 3.7	25/pkg	14551-68
Buffer Powder Pillows, pH 8.3	25/pkg	898-68
Hydrogen Peroxide Solution, 30%	200 mL MDB	144-45
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB*	323-32

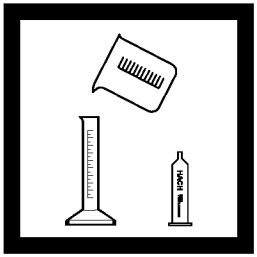
* Contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Hot Plate, 3½-inch circular, 115 V	each	12067-01
Hot Plate, variable control, 4-inch circular, 230 V	each	12067-02
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion***™*1* Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-0

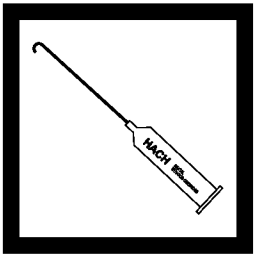
ALKALINITY (10 to 4000 mg/L as $CaCO_3$)

Phenolphthalein and Total Method

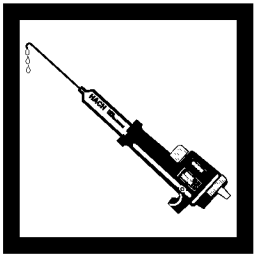


1. Select the sample volume and Sulfuric Acid (H_2SO_4) Titration Cartridge corresponding to the expected alkalinity concentration as mg/L calcium carbonate ($CaCO_3$) from *Table 1*.

Note: *See Sampling and Storage following these steps.*

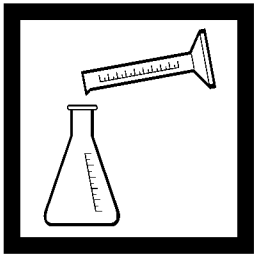


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

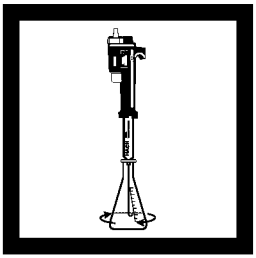
Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (H_2SO_4)	Catalog Number	Digit Multiplier
10-40	100	0.1600	14388-01	0.1
40-160	25	0.1600	14388-01	0.4
100-400	100	1.600	14389-01	1.0
200-800	50	1.600	14389-01	2.0
500-2000	20	1.600	14389-01	5.0
1000-4000	10	1.600	14389-01	10.0

5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.

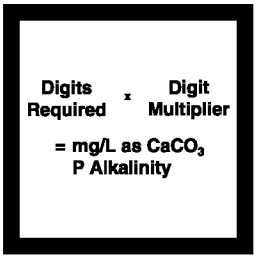
Note: *A solution of one pH 8.3 Buffer Powder Pillow and one Phenolphthalein Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.*

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*



6. If the solution turns pink, titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required.

Note: *If the solution is colorless before titrating with sulfuric acid, the Phenolphthalein (P) Alkalinity is zero; proceed with step 8.*



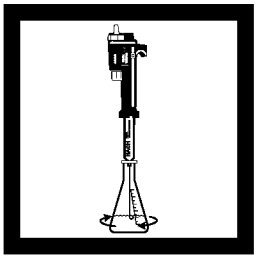
7. Calculate:

Digits Required x Digit Multiplier = mg/L $CaCO_3$ P Alkalinity

8. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the flask and swirl to mix.

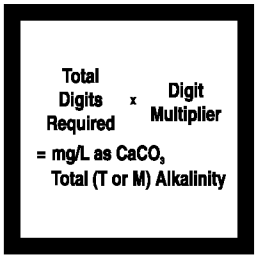
Note: *Four drops of Methyl Purple Indicator Solution may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow. Titrate from green to a gray end point (pH 5.1).*

Note: *Four drops of Bromcresol Green-Methyl Red Indicator Solution may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow.*



9. Continue the titration with sulfuric acid to a light greenish blue-gray (pH 5.1), a light violet-gray (pH 4.8), or a light pink (pH 4.5) color, as required by the sample composition; see *Table 2*. Record the number of digits required.

Note: *A solution of one Bromcresol Green-Methyl Red Powder Pillow and one pillow of the appropriate pH buffer in 50 mL of deionized water is recommended as a comparison for judging the proper end point color. If the pH 3.7 end point is used, use a Bromphenol Blue Powder Pillow instead of a Bromcresol Green-Methyl Red and titrate to a green end point.*



10. Calculate:

Total Digits Required x Digit Multiplier = mg/L as CaCO3 Total (T or M) Alkalinity

Note: *Carbonate, bicarbonate and hydroxide concentrations may be expressed individually using the relationships shown in Table 3.*

Note: *meq/L Alkalinity = mg/L as $CaCO_3$ ÷ 50.*

Table 2

Sample Composition	End Point
Alkalinity about 30 mg/L	pH 4.9
Alkalinity about 150 mg/L	pH 4.6
Alkalinity about 500 mg/L	pH 4.3
Silicates or Phosphates present	pH 4.5
Industrial waste or complex system	pH 4.5

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before analyzing.

Alkalinity Relationship Table

Total alkalinity primarily includes hydroxide, carbonate and bicarbonate alkalinities. The concentration of these alkalinities in a sample may be determined when the phenolphthalein and total alkalinities are known (see *Table 3*).

Table 3 Alkalinity Relationship

Row	Result of Titration	Hydroxide Alkalinity is equal to:	Carbonate Alkalinity is equal to:	Bicarbonate Alkalinity is equal to:
1	Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one half of Total Alkalinity	0	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one half of Total Alkalinity	2 times the Phenolphthalein minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

To use the table follow these steps:

a. Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.

b. Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.

c. Multiply the phenolphthalein alkalinity by 2.

d. Select Row 3, 4, or 5 based on comparing the result of *step c* with the total alkalinity.

e. Perform the required calculations in the appropriate row, if any.

f. Check your results. The sum of the three alkalinity types will equal the total alkalinity.

For example:
A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity. What is the concentration of hydroxide, carbonate and bicarbonate alkalinities?

The phenolphthalein alkalinity does not equal 0 (it is 170 mg/L), see *step a*.

The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L), see *step b*.

The phenolphthalein alkalinity multiplied by 2 = 340 mg/L, see *step c*.

Because 340 mg/L is greater than 250 mg/L, select Row 5, see *step d*.

The hydroxide alkalinity is equal to: (see *step e*).

340 – 250 = 90 mg/L hydroxide alkalinity

The carbonate alkalinity is equal to:

250 – 170 = 80
80 x 2 = 160 mg/L carbonate alkalinity

The bicarbonate alkalinity equals 0 mg/L.

Check: (see *step f*).

90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity +
0 mg/L bicarbonate alkalinity = 250 mg/L

The above answer is correct; the sum of each type equals the total alkalinity.

Accuracy Check

Standard Additions Method
This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off an Alkalinity Standard Solution Voluette® Ampule, 0.500 N.
2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in Steps 6 or 9. Resume titration back to the same end point. Record the number of digits needed.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 25 additional digits of 1.600 N titrant or 250 digits of 0.1600 N titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples.
- Chlorine may interfere with the indicators. Add one drop of 0.1 N Sodium Thiosulfate to eliminate this interference.

Summary of Method

The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titration to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator, and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 3.7 and 5.1, and includes all carbonate, bicarbonate and hydroxide.

REQUIRED REAGENTS
(varies with sample characteristics)

Description	Unit	Cat. No
Alkalinity Reagent Set (about 100 tests)		22719-00
Includes: (1) 942-99, (1) 943-99, (1) 14388-01, (1) 14389-01		
Bromcresol Green-Methyl Red Powder Pillows	100/pkg	943-99
Phenolphthalein Powder Pillows	100/pkg	942-99
Sulfuric Acid Titration Cartridge, 1.600 N	each	14389-01
Sulfuric Acid Titration Cartridge, 0.1600 N	each	14388-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Alkalinity Standard Solution Voluette® Ampules, 0.500 N Na_2CO_3, 10-mL	16/pkg	14278-10
Bromcresol Green-Methyl Red Indicator Solution	100 mL MDB	23292-32
Bromphenol Blue Indicator Solution	100 mL MDB	14552-32
Bromphenol Blue Powder Pillows	100/pkg	14550-99
Buffer Powder Pillows, pH 3.7	25/pkg	14551-68
Buffer Powder Pillows, pH 4.5	25/pkg	895-68
Buffer Powder Pillows, pH 4.8	25/pkg	896-68
Buffer Powder Pillows, pH 5.1	25/pkg	897-68
Buffer Powder Pillows, pH 8.3	25/pkg	898-68
Methyl Purple Indicator Solution	100 mL MDB	21934-32
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB	323-32

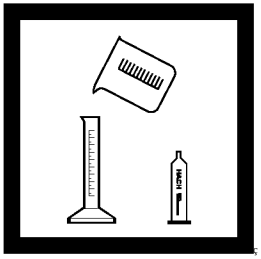
* Contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Unit	Cat. No
Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, TenSette® 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion**™1* Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

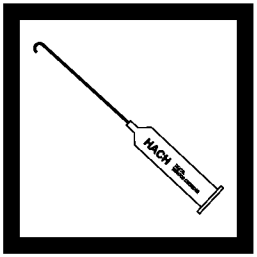
CARBON DIOXIDE (10 to 1000 mg/L as CO_2)

Using Sodium Hydroxide

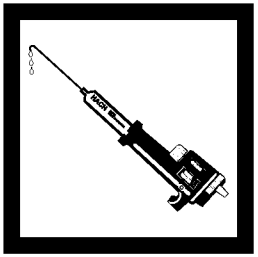


1. Select a sample size and a Sodium Hydroxide (NaOH) Titration Cartridge corresponding to the expected carbon dioxide (CO_2) concentration; see *Table 1*.

Note: *See Sampling and Storage following these steps.*



2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

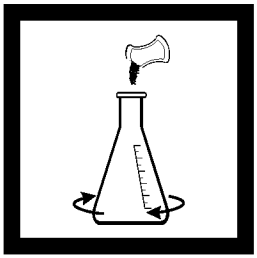
4. Collect a water sample directly into the titration flask by filling to the appropriate mark.

Note: *Minimize agitation because carbon dioxide may be lost.*

Note: *For most accurate results, check the calibration of the Erlenmeyer flask by measuring the proper volume in a graduated cylinder. Mark the proper volume on the flask with a permanent marker.*

Table 1

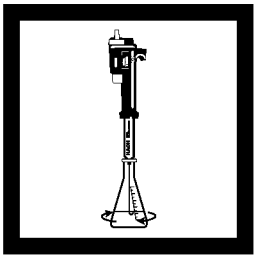
Range (mg/L as CO_2)	Sample Volume (mL)	Titration Cartridge (N NaOH)	Catalog Number	Digit Multiplier
10-50	200	0.3636	14378-01	0.1
20-100	100	0.3636	14378-01	0.2
100-400	200	3.636	14380-01	1.0
200-1000	100	3.636	14380-01	2.0



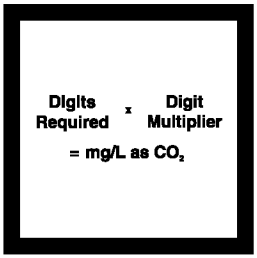
5. Add the contents of one Phenolphthalein Indicator Powder Pillow and mix.

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*

Note: *If a pink color forms, no carbon dioxide is present.*



6. Place the delivery tube tip into the solution and swirl the flask gently while titrating with sodium hydroxide from colorless to a light pink color that persists for 30 seconds. Record the number of digits required.



7. Calculate:

Total Digits Required x Digit Multiplier = mg/L as CO2

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples as soon as possible after collection. If immediate analysis is not possible, the samples may be stored for at least 24 hours by cooling to 4 °C (39 °F) or below. Before analysis, warm the samples to room temperature.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Carbon Dioxide Standard Solution Voluette® Ampule, 10,000 mg/L CO_2.

2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in *step 6*. If using 0.3636 N titrant, use 1.0 mL of standard. Resume titration back to the same end point. Record the number of digits required.

3. Repeat, using additions of 0.2 mL and 0.3 mL (2.0 and 3.0). Titrate to the same end point after each addition.

4. Each addition of standard should require 50 additional digits of titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- Other acid components in the sample will be titrated and interfere directly in this determination.

- Sodium hydroxide standard solutions tend to lose strength slowly with age and should be checked periodically by titrating a known standard. Check the solution frequently (monthly) by titrating 50 mL of Potassium Acid Phthalate Standard Solution, 100 mg/L CO_2, using Phenolphthalein Indicator Solution. The titration should require 5.00 mL of titrant. If the volume required for this titration is greater than 5.25 mL, discard the sodium hydroxide and replace it with a fresh supply.

Summary of Method

Acidity due to carbon dioxide in a sample is titrated with sodium hydroxide to a phenolphthalein end point. Strong acids are assumed to be absent or of insignificant concentration. Request Hach's *Water Analysis Handbook,* Publication 8376, to obtain additional information on carbon dioxide determinations.

REQUIRED REAGENTS
(varies with sample characteristics)

Description	Unit	Cat. No.
Carbon Dioxide Reagent Set (about 100 tests)		22727-00
Includes: (1) 942-99, (1) 14378-01, (1) 14380-01		
Phenolphthalein Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 0.3636 N	each	14378-01
Sodium Hydroxide Titration Cartridge, 3.636 N	each	14380-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Select one or more based on sample concentration:		
Flask, Erlenmeyer, 250 mL	each	505-46
Flask, Erlenmeyer, 125 mL	each	505-43

OPTIONAL REAGENTS

Carbon Dioxide Standard Solution Voluette® Ampules, 10,000 mg/L as CO_2, 10 mL	16/pkg	14275-10
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Potassium Acid Phthalate Standard Solution, 100 mg/L as CO_2	100 mL	2261-42
Potassium Acid Phthalate Standard Solution, 400 mg/L as CO_2	500 mL	1885-49

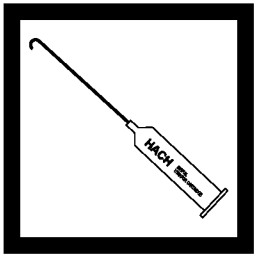
OPTIONAL APPARATUS

Clamp, 2-prong extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet Filler, safety bulb	each	14651-00
*sens**ion**™1* Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

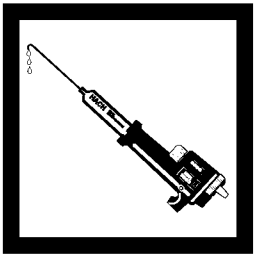
* Contact Hach for larger sizes.

CHELANT, FREE (0 to 20.0 mg/L as $CaCO_3$)

Using Magnesium Chloride

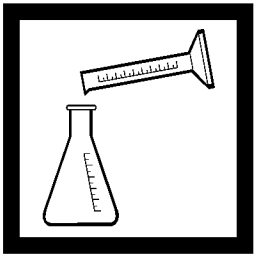


1. Insert a clean delivery tube into the Magnesium Chloride Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-By-Step,* for assembly instructions.



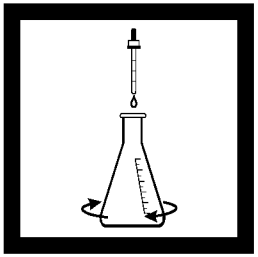
2. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



3. Use a graduated cylinder to measure the 100 mL of sample into a 125-mL Erlenmeyer flask.

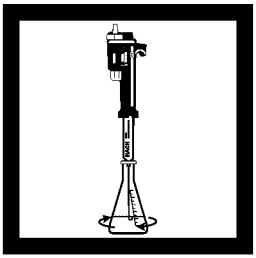
Note: *Filter sample if necessary. If sample is boiler water or highly alkaline, refer to Interferences following these steps.*



4. Using the 1-mL calibrated dropper, add 2 mL of Hardness 1 Buffer Solution to the flask and swirl to mix.

5. Add the contents of one ManVer® 2 Hardness Indicator Powder Pillow to the flask and swirl to mix. If the solution turns blue, free chelant is present. Proceed to *step 6*. If the solution turns red, a deficiency of chelant exists.

Note: *Four drops of ManVer Hardness Indicator Solution or a 0.1 g scoop of ManVer 2 Hardness Indicator Powder may be substituted in this step.*



6. Place the delivery tube tip into the solution. While swirling the flask, titrate until a red-violet color appears. Record the number of digits required.

7. Calculate:

Digits Required x 0.10 = mg/L Free Chelant (as $CaCO_3$)

Note: *The results may be expressed as mg/L tetra-sodium EDTA (digits required x 0.38 = mg/L as Na_4 EDTA).*

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Use a TenSette® Pipet to add 0.4 mL of 0.035 N EDTA Standard Solution to the solution titrated in *step 6*. Resume titration back to the same end point. Record the number of digits required.

2. Each 0.4 mL addition of standard should require 70 additional digits of 0.0800 M titrant. If this increase does not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- If chelant residual in boiler water is being analyzed, adjust the pH before adding the Hardness 1 Buffer Solution as follows:

  a. To another 100-mL sample, add 2 drops of Phenolphthalein Indicator Solution.

  b. Counting the drops, add 5.25 N Sulfuric Acid Standard Solution one drop at a time until the solution changes from pink to colorless. Discard this sample.

  c. To the actual 100-mL sample, add the same number of drops of 5.25 N Sulfuric Acid Standard Solution before adding the buffer in *step 4*.

- Orthophosphate causes a slow end point. Polyphosphate must be absent for accurate results.

- All apparatus must be scrupulously clean and rinsed frequently with acid and deionized water to remove any hardness present on the plastic or glass.

- Run reagent blanks occasionally, using deionized or distilled water in place of the sample. Subtract the value of the blank from the sample value before recording the final answer.

Summary of Method

Chelant residual is determined by titration with a standard solution of magnesium chloride at pH 10. The end point is determined by a color change from blue to red-violet.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Hardness 1 Buffer Solution	100 mL MDB	424-32
ManVer® 2 Hardness Indicator Powder Pillows	100/pkg	851-99
Magnesium Chloride Titration Cartridge, 0.0800 M	each	20625-01

REQUIRED APPARATUS

Cylinder, graduated, 100-mL	each	508-42
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43

OPTIONAL REAGENTS

EDTA Standard Solution, 0.035 N	100 mL MDB	23499-32
ManVer® 2 Hardness Indicator Powder	113 g	280-14
ManVer® 2 Hardness Indicator Solution	100 mL MDB*	425-32
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 L	272-56

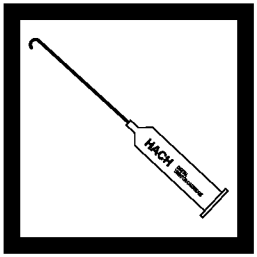
OPTIONAL APPARATUS

Clamp, 2-prong extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Clippers (shears), 7.25 inch	each	23694-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, Erlenmeyer, 250 mL	each	505-46
Funnel, analytical, poly, 65 mm	each	1083-67
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Spoon, measuring, 0.5 gram	each	907-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

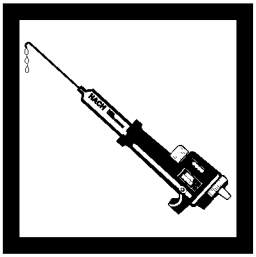
* Contact Hach for larger sizes.

CHELANT, TOTAL (0 to 40.0 mg/L as Na_4EDTA)

Using Bismuth Nitrate

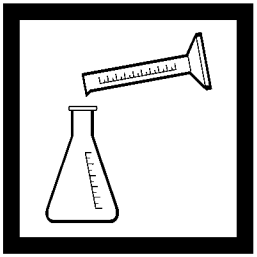


1. Insert a clean delivery tube into the Bismuth Nitrate Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-By-Step,* for assembly instructions.



2. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

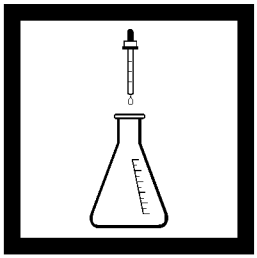


3. Use a graduated cylinder to measure the 50 mL of clear sample into a 125-mL Erlenmeyer flask.

Note: *Filtration is required for turbid samples.*

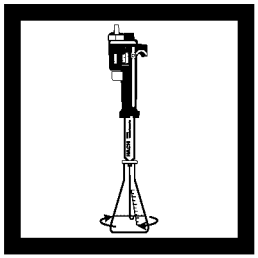
4. Add the contents of one Ascorbic Acid Powder Pillow to the flask and swirl to mix.

5. Add the contents of one Methylthymol Blue Powder Pillow to the flask and swirl to mix.



6. If the solution in the flask is yellow, add one drop of 5.25 N Sulfuric Acid Standard Solution.

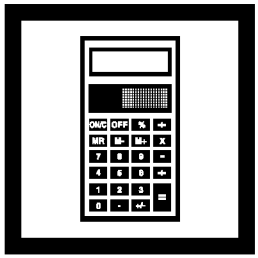
If the solution is blue, add 5.25 N Sulfuric Acid Standard Solution dropwise until the solution changes to yellow. Add one additional drop.



7. Place the delivery tube tip into the solution. While swirling the flask, titrate with the Bismuth Nitrate until the color changes from yellow to blue-green. Record the number of digits required.

Note: *Titrate slowly as the end point is approached.*

Note: *For best results, determine a reagent blank. Use 50 mL of deionized water in step 3. Subtract the number of digits required for the reagent blank from the number of digits required for titrating the sample.*



8. Calculate the final concentration:

Digits Required x 0.095 = Total Chelant (as mg/L Na_4EDTA)

Interferences

Interference from ferric iron (Fe^{3+}) is minimized by adding ascorbic acid. The end point should by approached slowly in samples containing ferric iron because the iron decreases the sharpness of the color change.

Summary of Method

Total chelant is determined by titrating an acid sample with bismuth nitrate the presence of methylthymol blue indicator. The end point is signaled by a color change from yellow to blue-green.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Ascorbic Acid Powder Pillows	100/pkg	14577-99
Bismuth Nitrate Titration Cartridge, 0.0200 M	each	24345-01
Methylthymol Blue Indicator Powder Pillows	50/pkg	22847-99
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32

REQUIRED APPARATUS

Cylinder, graduated, poly, 100 mL	each	1081-42
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Stir Bar, analytical, Teflon-coated, 50 mm	each	20953-55
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

OPTIONAL REAGENTS

Water, deionized	4 L	272-56

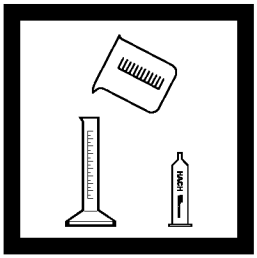
OPTIONAL APPARATUS

Clamp, 2-prong extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Clippers (shears), 7.25 inch	each	23694-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Filter paper, folded, 12.5 cm	100/pkg	1894-57
Flask, Erlenmeyer, 250 mL	each	505-46
Funnel, analytical, poly, 65 mm	each	1083-67

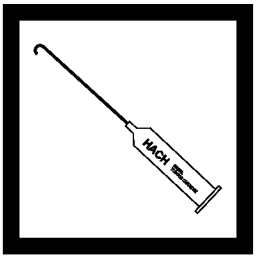
CHLORIDE

Mercuric Nitrate and Silver Nitrate Methods

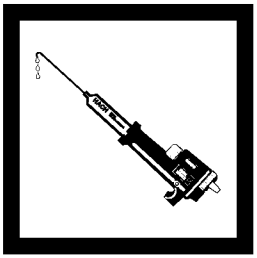
Mercuric Nitrate Method (10 to 8000 mg/L as Cl^-) Method 8206



1. Select the sample volume and Mercuric Nitrate Titration Cartridge corresponding to the expected chloride concentration from *Table 1*.

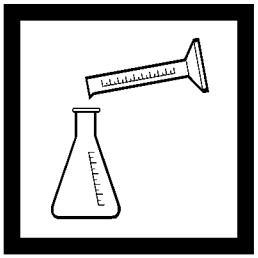


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description Section, Step-by-Step,* for assembly instructions if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

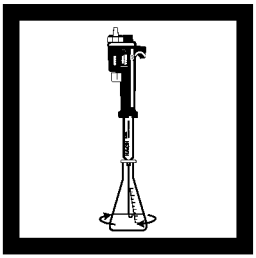
Note: *See following these steps.*

Table 1

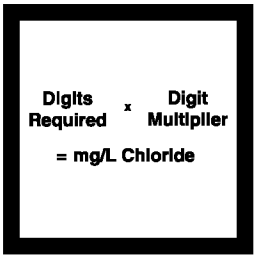
Range (mg/L as Cl^-)	Sample Volume (mL)	Titration Cartridge (N $Hg(NO_3)_2$)	Catalog Number	Digit Multiplier
10-40	100	0.2256	14393-01	0.1
40-160	25	0.2256	14393-01	0.4
100-400	100	2.256	921-01	1.0
200-800	50	2.256	921-01	2.0
500-2000	20	2.256	921-01	5.0
1000-4000	10	2.256	921-01	10.0
2000-8000	5	2.256	921-01	20.00

5. Add the contents of one Diphenylcarbazone Powder Pillow and swirl to mix.

Note: *Results will still be accurate if a small amount of the powder does not dissolve.*



6. Place the delivery tube tip into the solution and swirl the flask while titrating with mercuric nitrate from a yellow to light pink color. Record the number of digits required.



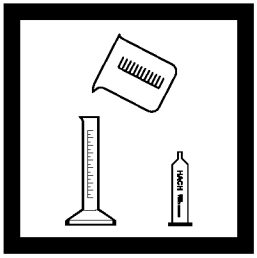
7. Calculate:

Digits Required x Digit Multiplier = mg/L Chloride

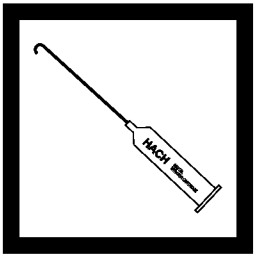
Note: *Results may be expressed as mg/L sodium chloride by multiplying the mg/L chloride by 1.65.*

Note: *meq/L Chloride = mg/L Cl^- ÷ 35.45.*

Silver Nitrate Method (10 to 10000 mg/L as Cl^-) Method 8207



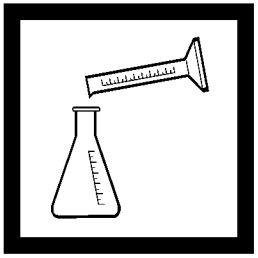
1. Select the sample volume and Silver Nitrate Titration Cartridge corresponding to the expected chloride concentration from *Table 2*.



2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description Section, Step-by-Step,* for assembly instructions if necessary.

3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

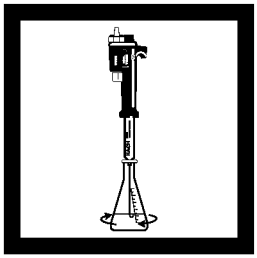
Note: *See following these steps.*

Table 2

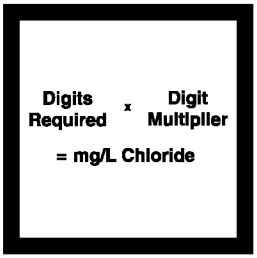
Range (mg/L as Cl^-)	Sample Volume (mL)	Titration Cartridge (N $AgNO_3$)	Catalog Number	Digit Multiplier
10-40	100	0.2256	14396-01	0.1
25-100	40	0.2256	14396-01	0.25
100-400	50	1.128	14397-01	1.0
250-1000	20	1.128	14397-01	2.5
1000-4000	5	1.128	14397-01	10.0
2500-10000	2	1.128	14397-01	25.0

5. Add the contents of one Chloride 2 Indicator Powder Pillow and swirl to mix.

Note: *Results will still be accurate if a small amount of the powder does not dissolve.*



6. Place the delivery tube tip into the solution and swirl the flask while titrating with silver nitrate from a yellow to red-brown color. Record the number of digits required.



7. Calculate:

Digits Required x Digit Multiplier = mg/L Chloride

Note: *Results may be expressed as mg/L sodium chloride by multiplying the mg/L chloride by 1.65.*

Note: *meq/L Chloride = mg/L Cl^- ÷ 35.45.*

Sampling and Storage

Collect at least 100 to 200 mL of sample in a clean glass or polyethylene container. Samples may be stored up to 7 days before analysis.

Accuracy Check

Standard Additions Method
This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Chloride Standard Solution Voluette® Ampule, 12,500 mg/L Cl^-.

2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample after titration in *step 6*. Resume titration back to the same end point. Record the number of digits required.

3. Repeat, using additions of 0.2 and 0.3 mL. Titrate to the end point after each addition.

4. Each 0.1 mL addition of standard should require 12.5 additional digits of 2.256 N titrant, 25 digits of 1.128 N titrant, or 125 digits of 0.2256 N titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences Using the Mercuric Nitrate Method

- Chromate, ferric iron, and sulfite in excess of 10 mg/L interfere with this method.

- Eliminate sulfite interference by adding three drops of hydrogen peroxide, 30%, in *step 4*.

- Remove sulfide interference by adding the contents of one Sulfide Inhibitor Reagent Powder Pillow to about 125 mL of sample, mixing for one minute, and filtering through a folded filter paper.

- Iodide and bromide interfere directly and titrate as chloride.

- Neutralize strongly alkaline or acid samples to a pH of 2 to 7 with 5.25 N Sulfuric Acid Standard Solution or 5.0 N Sodium Hydroxide Standard Solution. Determine the amount of acid or base necessary in a separate sample because pH electrodes will introduce chloride into the sample.

Interferences Using the Silver Nitrate Method

- Iron in excess of 10 mg/L masks the end point.
- Orthophosphate in excess of 25 mg/L will precipitate the silver.
- Sulfite in excess of 10 mg/L interferes. Eliminate sulfite interference by adding three drops of 30% hydrogen peroxide in *step 4*.
- Remove sulfide interference by adding the contents of one Sulfide Inhibitor Reagent Powder Pillow to about 125 mL of sample, mixing for one minute, and filtering through a folded filter paper.
- Cyanide, iodide, and bromide interfere directly and titrate as chloride.
- Neutralize strongly alkaline or acid samples to a pH of 2 to 7 with 5.25 N Sulfuric Acid Standard Solution or 5.0 N Sodium Hydroxide Standard Solution. Determine the amount of acid or base necessary in a separate sample because pH electrodes will introduce chloride into the sample.

Summary of the Mercuric Nitrate Method

When using Mercuric Nitrate Standard Solution, the sample is titrated under acid conditions in the presence of diphenylcarbazone indicator. Upon addition of a slight excess of mercuric ion, a pink-purple complex is formed with the indicator, signaling the end point.

Summary of the Silver Nitrate Method

The sample is titrated with Silver Nitrate Standard Solution in the presence of potassium chromate (from the Chloride 2 Indicator Powder). The silver nitrate reacts with the chloride present to produce insoluble white silver chloride. After all the chloride has been precipitated, the silver ions react with the excess chromate present to form a red-brown silver chromate precipitate, marking the end point of the titration.

Request Hach's *Water Analysis Handbook,* Publication 8376, to obtain additional information on chloride determinations.

REQUIRED REAGENTS FOR THE MERCURIC NITRATE METHOD

Description	Unit	Cat. No.
Mercuric Nitrate Chloride Reagent Set (about 100 tests)		22726-00
Includes: (2) 836-46, (1) 921-01, (1) 14393-01		
Diphenylcarbazone Reagent Powder Pillows	100/pkg	836-99
Mercuric Nitrate Titration Cartridge, 0.2256 N	each	14393-01
Mercuric Nitrate Titration Cartridge, 2.256 N	each	921-01
Water, deionized	4 L	272-56

REQUIRED REAGENTS FOR THE SILVER NITRATE METHOD

Silver Nitrate Chloride Reagent Set (about 50 tests)		22880-00
Includes: (2) 1057-66, (1) 14396-01, (1) 14397-01		
Chloride 2 Indicator Powder Pillows	50/pkg	1057-66
Silver Nitrate Titration Cartridge, 0.2256 N	each	14396-01
Silver Nitrate Titration Cartridge, 1.128 N	each	14397-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS FOR THE MERCURIC NITRATE METHOD AND SILVER NITRATE METHOD

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

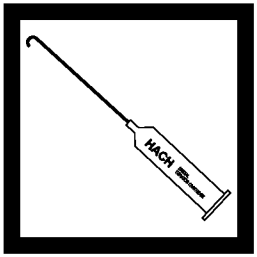
Chloride Standard Solution, 1000 mg/L Cl^-	500 mL	183-49
Chloride Standard Solution Voluette® Ampules, 12,500 mg/L Cl^-, 10-mL	16/pkg	14250-10
Hydrogen Peroxide, 30%, ACS	200 mL	144-45
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sulfide Inhibitor Powder Pillows	100/pkg	2418-99
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32

OPTIONAL APPARATUS

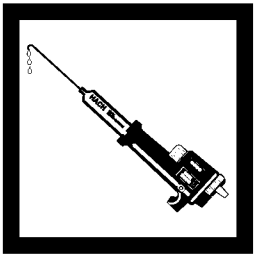
Description	Unit	Cat. No.
Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Funnel, poly, 65-mm	each	1083-67
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 2-mL	each	14515-36
Pipet, volumetric, Class A, 5-mL	each	14515-37
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion**™1* Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

CHLORINE, FREE AND TOTAL (0 to 3.00 mg/L as Cl_2)

DPD-FEAS Method

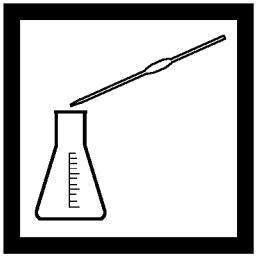


1. Insert a clean delivery tube into a 0.00564 N Ferrous Ethylenediammonium Sulfate (FEAS) Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step*, for assembly instructions, if necessary.



2. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

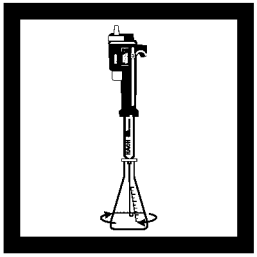


3. Pipet 25.0 mL of sample into a 50-mL Erlenmeyer flask.

4. Add the contents of a DPD Free Chlorine Powder Pillow to the sample and swirl to mix.

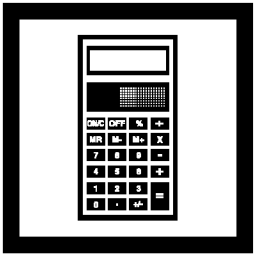
Note: *Accuracy is unaffected if a small portion is undissolved.*

Note: *See Sampling and Storage following these steps.*



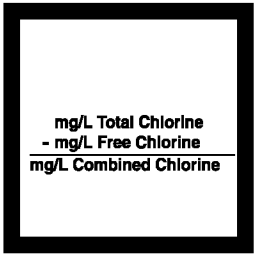
5. Place the delivery tube tip into the solution and swirl the flask while immediately titrating with FEAS to a colorless end point. Record the number of digits required.

Note: *Complete the titration rapidly.*



6. Calculate:

Digits Required x 0.01 = mg/L Free Chlorine



7. If total residual chlorine is desired, return to *step 3* and substitute a DPD Total Chlorine Powder Pillow in *step 4*. Wait three minutes before titrating. Continue with *step 5*. The results will be expressed as mg/L total chlorine.

mg/L Total Chlorine - mg/L Free Chlorine = mg/L Combined Chlorine

Sampling and Storage

Chlorine in water is easily lost. Therefore, start chlorine determinations immediately after sampling, avoiding excessive light and agitation. Do not store samples.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when the analyst suspects interferences or to verify analytical technique.

1. Snap the neck off a Chlorine Standard Solution PourRite™ Ampule.
2. Use a TenSette® Pipet to add 0.10 mL, 0.20 and 0.30 mL of standard, respectively, to three 25-mL samples. Mix each well.
3. Analyze each sample as described in the procedure.
4. Each 0.1-mL addition of standard should require approximately 20 digits. Check the certificate enclosed with the PourRite Ampules to obtain the exact concentration. To determine the exact number of digits required for each 0.2-mL addition, multiply the exact concentration times the volume of the addition in mL times four. (Example: 50 mg/L x 0.1 mL x 4 = 20 digits.) If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

Higher room temperatures tend to lead to higher free chlorine residual due to reaction of chloramines. Higher room temperatures also result in increased color fading. If the sample contains more than 250 mg/L alkalinity or 150 mg/L acidity as $CaCO_3$, the sample may not develop the full amount of color or it may instantly fade. To overcome this interference, adjust the pH of a separate 25-mL sample to a 6 to 7 pH by adding 1 N Sulfuric Acid Standard Solution or 1 N Sodium Hydroxide Standard Solution in small increments and using a pH meter. Record the amount of acid or base required. Add this amount of acid or base to the sample to be tested and proceed with *step 4*.

Bromine, iodine, ozone, and oxidized forms of manganese and chromium will also react and read as chlorine. To compensate for the effects of manganese, Mn^{4+}, or chromium, Cr^{6+}, add three drops of Potassium Iodide, 30 g/L to 25 mL of sample. Mix and wait one minute. Add three drops of Sodium Arsenite, 5 g/L and mix. Analyze this solution as described above. (If chromium is present, allow exactly the same reaction period in *step 7* with the DPD for both analyses.) Subtract the result from the original analysis to correct for the interference.

Summary of Method

The DPD-FEAS method provides a titrimetric procedure for determining free available chlorine and for estimating free and combined chlorine fractions present together. The magenta species, resulting from the oxidation of DPD by chlorine, is destroyed quantitatively by titration with ferrous ethylenediammonium sulfate and the volume of titrant required to reach a colorless end point is proportional to the chlorine concentration. Total residual chlorine may also be determined by this test.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Free and Total Chlorine Reagent Set (about 100 tests)		24453-00
Includes: (1) 14064-99, (1) 14070-99, (1) 22923-01		
DPD Free Chlorine Powder Pillows, 25 mL	100/pkg	14070-99
DPD Total Chlorine Powder Pillows, 25 mL	100/pkg	14064-99
Ferrous Ethylenediammonium Sulfate Titration Cartridge, 0.00564 N	each	22923-01

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 50-mL	each	505-41
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet Filler, safety bulb	each	14651-00

OPTIONAL REAGENTS

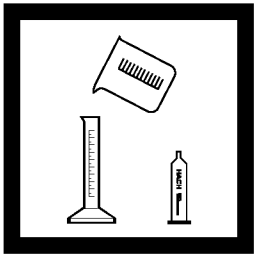
Chlorine Standard Solution, PourRite™ Ampules, 50-75 mg/L Cl_2, 2-mL	20/pkg	14268-20
Potassium Iodide Solution	100 mL MDB	343-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL MDB	1270-32
Sodium Hydroxide Standard Solution, 1.000 N	100 mL MDB	1045-32
Sodium Arsenite Solution	100 mL MDB	1047-32

OPTIONAL APPARATUS

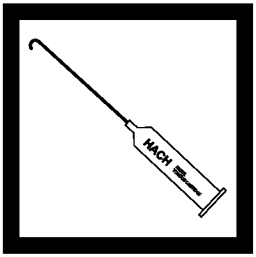
Clamp, 2-prong, extension	each	21145-00
Clamp Holder	each	326-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
PourRite™ Ampule Breaker	each	24846-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

CHLORINE, TOTAL

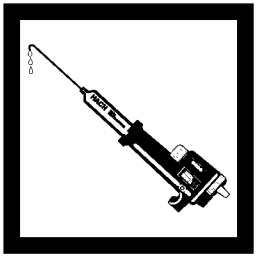
Iodometric Method (1 to 400 mg/L as Cl_2 Using Sodium Thiosulfate)



1. Select the sample volume and Sodium Thiosulfate Titration Cartridge corresponding to the expected chlorine concentration from *Table 1*.

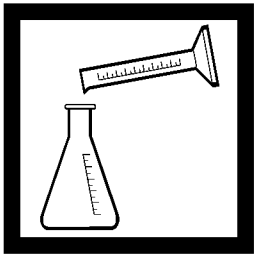


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step*, for assembly instructions, if necessary.



3. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a clean graduated cylinder to take a water sample. Pour sample into a clean 125- or 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water.

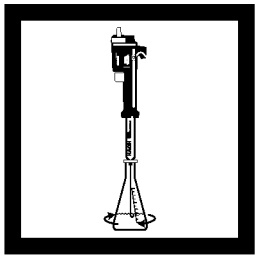
Note: *See Sampling and Storage following these steps.*

Table 1

Range (mg/L Cl_2)	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
1-4	100	0.02256	24091-01	0.01
2-8	50	0.02256	24091-01	0.02
5-20	20	0.02256	24091-01	0.05
10-40	10	0.02256	24091-01	0.10
20-80	5	0.02256	24091-01	0.20
50-200	2	0.02256	24091-01	0.50
100-400	1	0.02256	24091-01	1.00

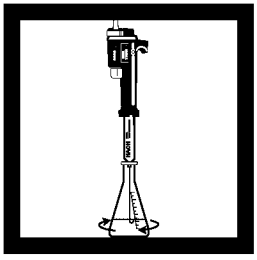
5. Add 2 Droppers (2 mL) Acetate Buffer Solution, pH 4 and swirl to mix.

6. Clip open the end of one Potassium Iodide Powder Pillow. Add the contents to the flask. Swirl to mix.

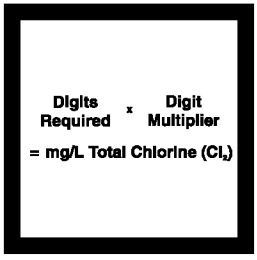


7. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate until the solution is a pale yellow.

8. Add one dropper of starch indicator solution and swirl to mix. A dark blue color will develop.



9. Continue the titration until the solution changes from dark blue to colorless. Record the number of digits required.



10. Calculate:

Digits Required x Digit Multiplier = mg/L Total Chlorine (Cl2)

Note: *These procedures can be used to check iodine and bromine concentrations if chlorine is not present. Multiply the test result (in mg/L chlorine) by 3.58 or 2.25, respectively, to accurately express the iodine or bromine content of your sample.*

Sampling and Storage

Collect at least 200 mL of sample in a clean glass or polyethylene container. Analyze on site or as soon as possible after collection.

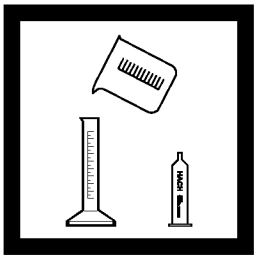
Accuracy Check

Standard Additions Method

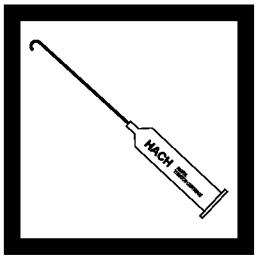
Perform this accuracy check when you suspect interferences or to verify analytical technique.

1. Snap the neck off a Chlorine Standard Solution PourRite™ Ampule.
2. Use a TenSette® Pipet to add 0.2 mL, 0.4 mL, and 0.6 mL of standard to three aliquots of sample of the same volume as used in the procedure.
3. Analyze each sample as described in the procedure.
4. Each 0.2-mL addition of standard should require approximately 10 digits of the titration cartridge solution. Check the certificate enclosed with the PourRite Ampules to obtain the exact concentration. To determine the exact number of digits required for each 0.2-mL addition, multiply the exact concentration times the volume of the addition in mL. (Example: 50 mg/L x 0.2 mL = 10 digits.) If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

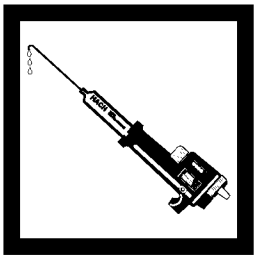
Iodometric Method (20 to 70,000 mg/L as Cl_2 Using Sodium Thiosulfate)



1. Select the sample volume and Sodium Thiosulfate Titration Cartridge corresponding to the expected chlorine concentration from *Table 2*.

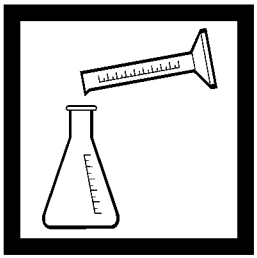


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step*, for assembly instructions, if necessary.



3. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TirtaStir® stirring apparatus. See General Description, Step 3 of Step-by-Step.*



4. Use a pipet or graduated cylinder to measure the sample volume from *Table 2*. Transfer the sample into a 125-mL Erlenmeyer flask and dilute to about the 50-mL mark with deionized water.

Table 2

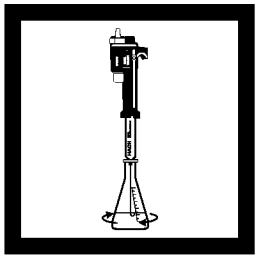
Range (mg/L Cl_2)	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
20-80	25	0.113	22673-01	0.2
50-200	10	0.113	22673-01	0.5
100-400	5	0.113	22673-01	1
250-1000	2	0.113	22673-01	2.5
500-2000	1	0.113	22673-01	5
2000-9000 (0.2-0.9%)	4	2.00	14401-01	22.2
5000-18,000 (0.5-1.8%)	2	2.00	14401-01	44.3
10,000-35,000 (1.0-3.5%)	1	2.00	14401-01	88.7
20,000-70,000 (2.0-7.0%)	0.5	2.00	14401-01	177

5. Add the contents of one Dissolved Oxygen 3 Powder Pillow.

Note: *Normally the addition of the powder pillow will lower the pH to 4 or less. If the sample size is large and highly alkaline, verify the solution pH is 4 or less with a pH meter or pH paper before proceeding.*

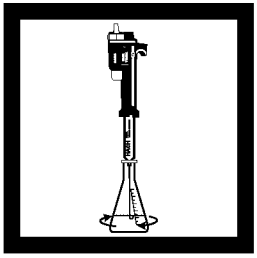
6. If you are using the 2.00 N titration cartridge, add the contents of one Potassium Iodide Powder Pillow (Cat. No. 20599-96) to the flask and swirl to mix.

If you are using the 0.113 N titration cartridge, add the contents of one Potassium Iodide Powder Pillow (Cat. No. 1077-99) to the flask and swirl to mix.

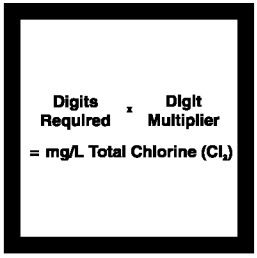


7. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate until the solution is a pale yellow.

8. Add one dropperful of starch indicator solution and swirl to mix. A dark blue color will develop.



9. Continue the titration until the solution changes from dark blue to colorless. Record the number of digits required.



10. Calculate:

Digits Required x Digits Multiplier = mg/L Total Chlorine (Cl2)

To convert the above results to the equivalent percent chlorine (Cl_2), divide by 10,000.

Accuracy Check

Standard Additions Method

This accuracy check is applicable **only for the 0.113 N titration cartridge**. Perform it when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Chlorine Standard Solution PourRite Ampule.
2. Use a TenSette Pipet (or glass pipet) to add 1.0 mL, 2.0 mL, and 3.0 mL of standard to three samples of the same volume as used in the procedure.
3. Analyze each sample as described in the procedure.
4. Each 1.0-mL addition of standard should require approximately 10 digits of the 0.113 N titration cartridge. Check the certificate enclosed with the PourRite Ampules to obtain the exact concentration. To determine the exact number of digits required for each 1.0-mL addition, multiply the exact concentration times the volume of the addition in mL. Divide this by five. For example: (50 mg/L x 1.0 mL) ÷ 5 = 10 digits. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Summary of Method

Total chlorine concentration equals the concentration of the free and the combined forms of chlorine. Free chlorine reacts readily with ammonia to form combined chlorine such as monochloramines. When potassium iodide is added to a sample containing chlorine at a pH less than 8, free iodine is liberated in direct proportion to the amount of total chlorine present. The iodine is then titrated with sodium thiosulfate.

REQUIRED REAGENTS (For Using the 0.02256 N Titration Cartridge)

Description	Unit	Cat. No.
Acetate Buffer Solution, pH 4	100 mL MDB	14909-32
Potassium Iodide Powder Pillows	100/pkg	1077-99
Starch Indicator Solution	100 mL MDB*	349-32
Sodium Thiosulfate Titration Cartridge, 0.02256 N	each	24091-01

REQUIRED REAGENTS (For Using the 0.113 N Titration Cartridge)

Chlorine Reagent Set, 20-2,000 mg/L (about 100 tests) Includes: (1) 349-32, (1) 987-99, (1) 1077-99, (1) 22673-01		22725-00
Dissolved Oxygen 3 Powder Pillows	100/pkg	987-99
Potassium Iodide Powder Pillows	100/pkg	1077-99
Sodium Thiosulfate Titration Cartridge, 0.113 N	each	22673-01
Starch Indicator Solution	100 mL MDB*	349-32
Water, deionized	4 L	272-56

REQUIRED REAGENTS (For Using the 2.00 N Titration Cartridge)

Chlorine Reagent Set, 2,000-70,000 mg/L (about 100 tests) Includes: (1) 349-32, (1) 987-99, (2) 14401-01, (2) 20599-96		24448-00
Dissolved Oxygen 3 Powder Pillows	100/pkg	987-99
Potassium Iodide Powder Pillows	50/pkg	20599-96
Sodium Thiosulfate Titration Cartridge, 2.00 N	each	14401-01
Starch Indicator Solution	100 mL MDB*	349-32
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Pipet Filler, 3-valve	each	12189-00
Select one or more based on sample concentration:		
Pipet, serological, 1 mL	each	532-35
Pipet, volumetric, Class A, 1 mL	each	14515-35
Pipet, volumetric, Class A, 2 mL	each	14515-36
Pipet, volumetric, Class A, 4 mL	each	14515-04
Pipet, volumetric, Class A, 5	each	14515-37
Pipet, volumetric, Class A, 10 mL	each	14515-38
Pipet, volumetric, Class A, 25 mL	each	14515-40

* Contact Hach for larger sizes.

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chlorine Standard Solution, PourRite™ Ampules, 50-75 mg/L as Cl_2, 2 mL	20/pkg	14268-20

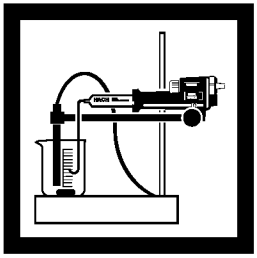
OPTIONAL APPARATUS

Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Cylinder, graduated, 5 mL	each	508-37
Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
pH Paper, 1-11 pH	5 rolls/pkg	391-33
PourRite™ Ampule Breaker	each	24846-00
*sens**ion**™1* Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

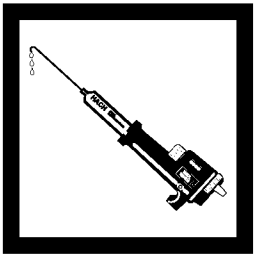
CHLORINE, FREE (0 to 1000 µg/L as Cl_2)

Amperometric Forward Titration

USEPA Accepted for Reporting*

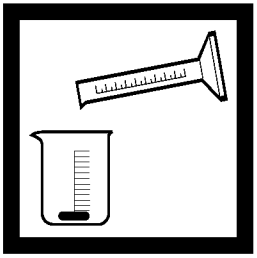


1. Assemble the Amperometric Digital Titrator System according to the instructions in the *Amperometric Titrator Instruction Manual*.



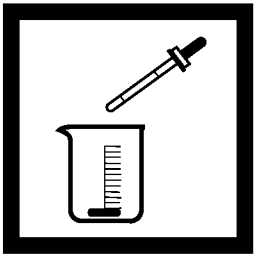
2. Install the 0.00564 N Phenylarsine Oxide (PAO) cartridge. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *When a new probe is placed in service or when the probe has not been used recently, prepare it according to the Probe Stabilization instructions in the Amperometric Titrator Instruction Manual.*



3. With minimum agitation, measure 200 mL of sample with a clean graduated cylinder. Transfer the sample to a clean 250-mL beaker containing the 50-mm stirring bar supplied with the system.

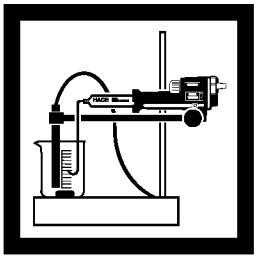
Note: *An improper stirring bar size can result in volatilization of chlorine, instability of readings and loss of sensitivity.*



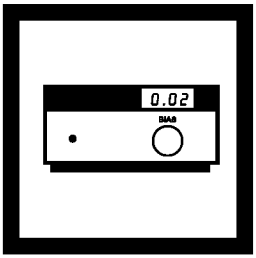
4. Add 1 mL of pH 7 Phosphate Buffer Solution.

Note: *If the sample pH is between 6.5 and 7.5 it is not necessary to add the buffer.*

* Procedure is equivalent to *Standard Methods for the Examination of Water and Wastewater* (18th ed.) 4500 Cl D for drinking water.

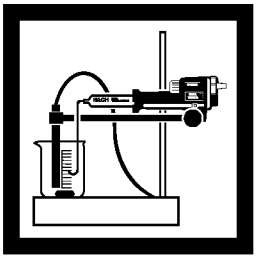


5. Place the beaker on the TitraStir® Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



6. Note the LED reading on the Amperometric Titrator. Unlock the BIAS control and adjust the BIAS control knob until a reading between 0.50-0.60 is obtained. Lock the BIAS control.

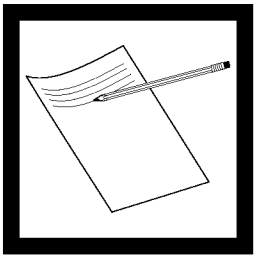
Note: *The bias adjustment controls the slope of the titration curve. The actual instrument reading is not important; but rather the change in the readings as the titration proceeds. The adjustment need not be precise.*



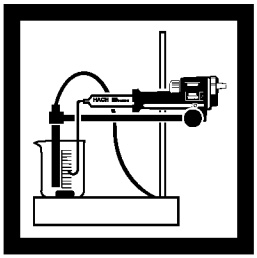
7. Using the Digital Titrator delivery knob, dispense the PAO titrant Solution in 5-10 digit increments while noting the LED reading.

Note: *If the chlorine content of the sample is high, add titrant at a faster rate; only the end point of the titration and the volume of titrant used at the end point are of concern. For example, if the chlorine content is approximately 500 µg/L, up to 300 digits of 0.00564 N PAO could be added at once. As the end point is approached, dispense in small increments.*

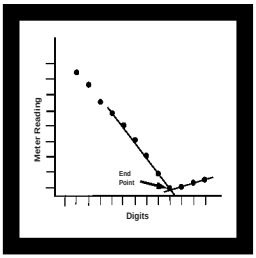
Note: *If excess reductant such as sulfite, bisulfite or sulfur dioxide is present in the sample, the LED readings will not decrease and may even increase. This indicates that no free chlorine is present in the sample*



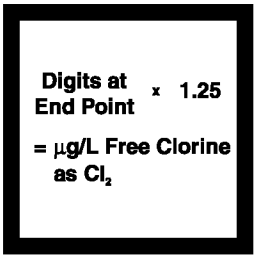
8. As the end point of the titration is approached, record the LED readings along with the corresponding digits displayed on the Digital Titrator counter. Near the titration end point, add 2 to 5 digits of titrant; wait a few seconds for a stable reading and record.



9. Continue the titration, recording at least three points on the downward sloping curve and at least three points after the end point has been reached. The latter points will have little change in the LED readings.



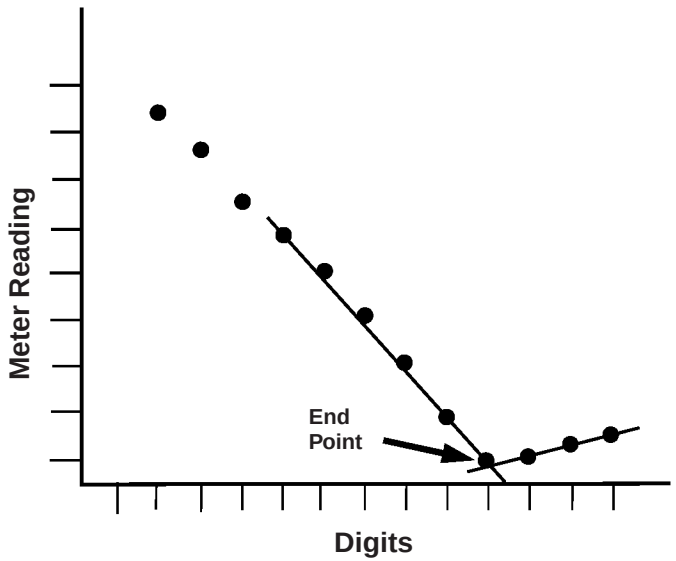
10. Using linear graph paper, plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the horizontal axis. Draw the two best intersecting lines through the points; see *Figure 1*. Determine the number of digits at the intersection of the lines; this is the end point.



11. Calculate the µg/L free chlorine:

Digits at End Point x 1.25 = µg/L free chlorine as Cl_2

Figure 1
Sample Plot



Accuracy Check

Standard Additions Method*

1. Snap the top off a Chlorine Standard Solution PourRite™ Ampule. Note the certificate value of the standard in mg/L.
2. Split a fresh sample into two 200-mL portions.
3. Using a TenSette® Pipet, add from 0.1 to 0.5 mL of the standard to one portion and swirl to mix. This is the *spiked sample*.
4. Analyze both the sample and spiked sample and record the chlorine concentration of each.
5. Calculate the theoretical concentration of the spiked sample:

$$\text{heoretical concentration} = \frac{(C_u \times V_u) + (C_s \times V_s)}{V_u + V_s}$$

Where:

C_u = measured concentration of sample, in mg/L (µg/L divided by 1000)

V_u = volume of sample in mL

C_s = concentration of chlorine standard (mg/L, certificate value)

V_s = volume of standard added in mL

6. Calculate the percent spiked recovery:

$$\text{Spike Recovery} = \frac{\text{Spiked sample result, in mg/L}}{\text{Theoretical concentration calculated, in mg/L}} \times 100$$

Example:

Sample result (C_u) = 120 µg/L or 0.120 mg/L

Spiked sample result = 185 µg/L or 0.185 mg/L

Volume Sample (V_u) = 200 mL

Volume Standard (V_s) = 0.2 mL

Chlorine Standard (C_s) = 68.1 mg/L

$$\text{heoretical concentration} = \frac{(0.120 \times 200) + (68.1 \times 0.2)}{200 + 0.2} = 0.188 \text{ mg/L}$$

$$\text{\% Spike recovery} = \frac{0.185 \text{ mg/L}}{0.188 \text{ mg/L}} \times 100 = 98\%$$

Ideally, the percent recovery should be 100%. Generally, results from 80-120% recovery are considered acceptable.

* The standard additions technique is not applicable for samples containing excess reducing agents such as sulfur dioxide, sulfite, or bisulfite.

Precision

In a single laboratory, using a standard solution of 338 µg/L chlorine, a single operator obtained a standard deviation of ± 5.2 µg/L chlorine.

Detection Limit

With good operator technique, the estimated detectable concentration is approximately 15 µg/L chlorine using 0.00564 N PAO.

Sampling and Storage

Chlorine is rapidly lost from water. Avoid exposure to sunlight or other strong light. Avoid excessive agitation. Analyze samples immediately.

Interferences

- Silver ions poison the electrode.
- Copper ions interfere.
- Interferences are sometimes found in highly turbid water and those containing surface active agents.
- Oxidized manganese and other oxidizing reagents give positive interferences.
- Some uncertainty in the end point may be observed with samples containing high organic content.
- Samples containing excess reducing agents, such as sulfur dioxide, sulfite, and bisulfite do not contain free chlorine and can not be titrated under the conditions of the test.
- Highly buffered samples or extreme sample pH may exceed the buffering capacity of the buffer reagent. If necessary, add additional buffer and check pH of sample prior to titration.

Summary of Method

In the amperometric forward titration procedure for free chlorine, a small electrical current is applied across two identical platinum electrodes. No current can flow between the electrodes unless a

substance that can be oxidized at the anode and a substance that can be reduced at the cathode are both present. In the case of the free chlorine titration with phenylarsine oxide (PAO), chlorine is reduced at the cathode to chloride due to the addition of PAO and PAO is oxidized from the +3 oxidation state to the +5 oxidation state at the anode. Prior to the end point of the titration, both free chlorine and chloride are present in solution; allowing current to flow, even with a very small applied potential. At the end point, no free chlorine remains and the solution cannot conduct even if excess PAO titrant is added. The end point is defined when no change in current occurs, signaling all free chlorine has been reacted.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Phenylarsine Oxide Solution, 0.00564 N Digital Titrator Cartridge	each	1999-01
Phosphate Buffer Solution, pH 7	100 mL MDB	21553-32

REQUIRED APPARATUS

Amperometric Titrator Assembly	each	19299-00
Digital Titrator	each	16900-01
Beaker, low-form, 250 mL	each	500-46
Cylinder, graduated, 250 mL	each	508-46
Delivery Tubes, 90° with hook	5/pkg	41578-00
Probe Assembly, Amperometric Titrator	each	19390-00
Stir Bar, octagonal, Teflon-coated, 50.8 x 7.9 mm	each	20953-55
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

OPTIONAL REAGENTS

Chlorine Standard Solution PourRite™ Ampules, 50-75 mg/L Cl_2, 2 mL	20/pkg	14268-20
Water, deionized	4 L	272-56

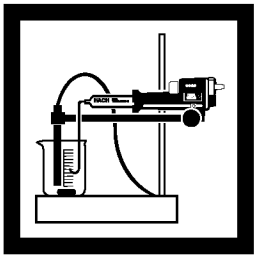
OPTIONAL APPARATUS

Pipet, TenSette® 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
PourRite™ Ampule Breaker	each	24846-00
Standard Methods for the Examination of Water and Wastewater, 19th edition	each	22708-00

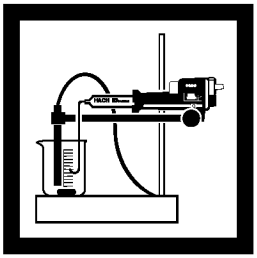
CHLORINE, TOTAL (6 to 1000 µg/L as Cl_2)

Amperometric Back Titration
USEPA Accepted for Reporting*

Phase 1: Adjusting the Electrode Response Slope

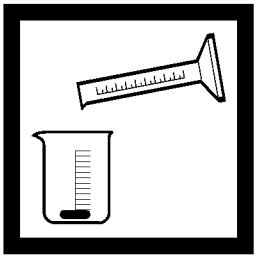


1. Assemble the Amperometric Digital Titrator System according to the instructions in the *Amperometric Titrator Instruction Manual*.



2. Install the Standard Iodine Titrant Cartridge, 0.028 N. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *When a new probe is used or the probe has not been used recently, prepare it according to the Probe Stabilization instructions in the Amperometric Titrator Instruction Manual.*

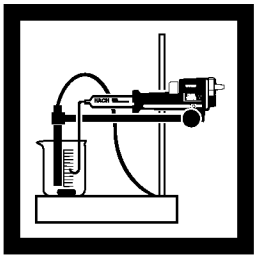


3. Using a graduated cylinder, measure 200 mL of deionized water into a clean 250-mL beaker. Place the 50-mm stirring bar supplied with the system into the beaker.

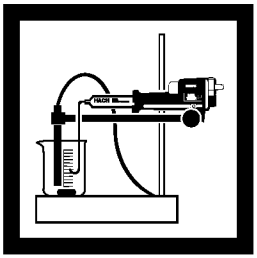
Note: *An improper size stirring bar can result in volatilization of iodine, instability of readings and loss of sensitivity.*

4. Add 1 mL of pH 4 Acetate Buffer and the contents of one Potassium Iodide Pillow.

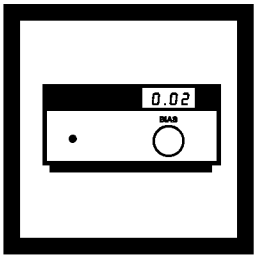
* Procedure is equivalent to USEPA method 330.2 and *Standard Methods for the Examination of Water and Wastewater* (17th ed.) 4500-Cl C for wastewater.



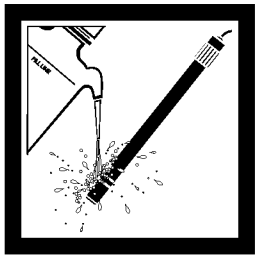
5. Place the beaker on the TitraStir® Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



6. Using the Digital Titrator delivery knob, add 50 digits of Standard Iodine Titrant Solution.

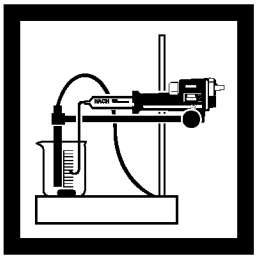


7. Note the LED reading on the Amperometric Titrator. Unlock the BIAS control and adjust the BIAS control knob until a stable reading between 0.50-0.60 is obtained. Lock the BIAS control.

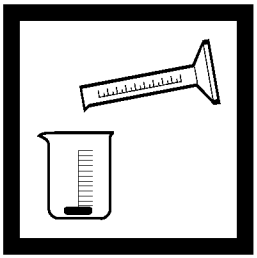


8. Remove the probe arm from the beaker and rinse the platinum wires with deionized water. Adjustment of the electrode response slope is complete.

Phase 2: Standardization of the Iodine Titrant

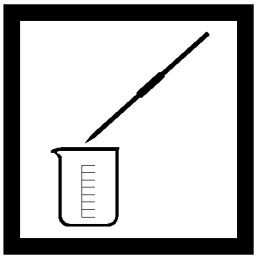


1. Set-up the Amperometric Digital Titrator System as in *Phase 1: Adjusting the Electrode Response Slope* if it has not already been done. Reset the Digital Titrator counter to zero and wipe the tip.



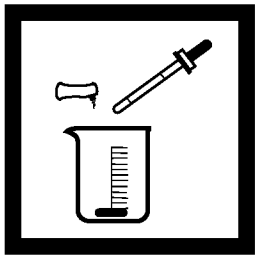
2. Using a graduated cylinder, measure 200 mL of deionized water into a clean 250-mL beaker. Place the 50-mm stirring bar supplied with the system into the beaker.

Note: *An improper size of stirring bar can result in volatilization of iodine, instability of readings and loss of sensitivity.*

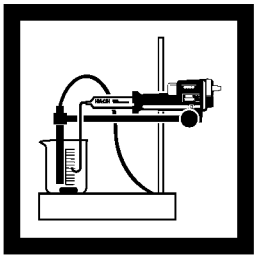


3. Using a Class A pipet, transfer 1.00 mL of 0.00564 N Sodium Thiosulfate Solution to the beaker. Swirl to mix.

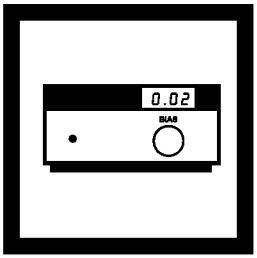
Note: *Alternatively, use 0.00564 N Phenylarsine Oxide (PAO), Cat. No. 1999, instead of thiosulfate.*



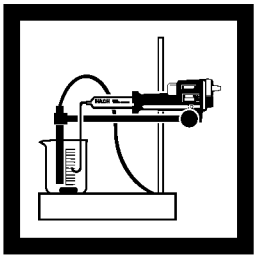
4. Add 1 mL of pH 4 Acetate Buffer Solution and the contents of one Potassium Iodide Powder Pillow.



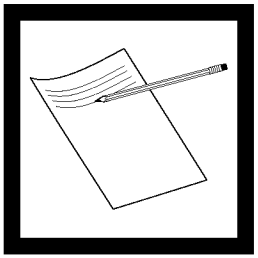
5. Place the beaker on the TitraStir Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



6. Note the LED reading on the Amperometric Titrator. It should read 0.00 ± 0.05. DO NOT adjust the BIAS control.

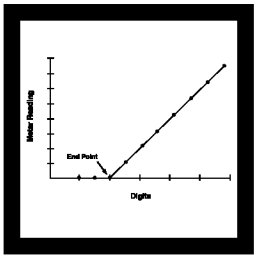


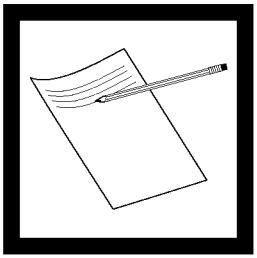
7. Using the Digital Titrator delivery knob, dispense 100 digits of Standard Iodine Titrant Solution and note the LED reading.

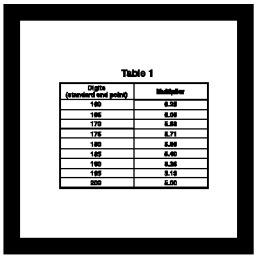


8. Continue dispensing titrant in 5-10 digit increments while noting the LED reading. Record at least 3 points (null current values and Digital Titrator reading), before the end point is reached. After the end point of the titration (nominal 160 digits), record the increasing LED readings along with the corresponding digits displayed on the Digital Titrator counter. Add 5-10 digits of titrant; wait a few seconds for a stable reading and record it. Stop adding titrant when the LED readings exceed 0.60.

Note: *LED readings above 0.60 will be excessively noisy.*







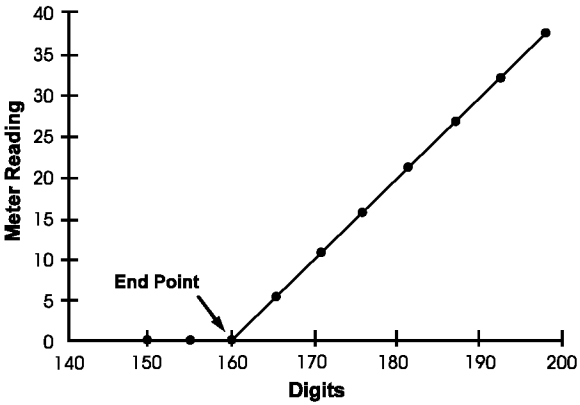
9. Using linear graph paper, plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the horizontal axis. Draw the two best intersecting lines through the points plotted. See *Figure 1*. Determine the number of digits at the intersection of the lines. This is the *standard* end point.

10. Record the standard end point digits value. This value will be used in calculation of the sample chlorine concentration.

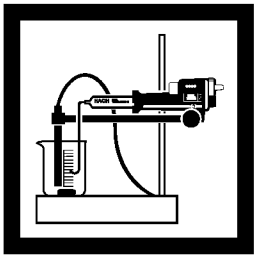
Note: *The iodine titrant concentration is approximately 0.0282 N, which relates to 160 digits needed to titrate 1.00 mL of 0.00564 N Thiosulfate. If the calculated end point is greater than 160 digits, this indicates the Standard Iodine Titrant is weaker than when packaged. Discard the Standard Iodine Titrant cartridge if the calculated standardization end point is greater than 200 digits.*

11. Locate the appropriate multiplier based on the standard end point in *Table 1* on page 93. The multiplier is used in *Phase 3: Titration of Sample for Total Residual Chlorine*. Interpolation between values in the table is not necessary.

igure 1
ack Amperometric
itration Graph



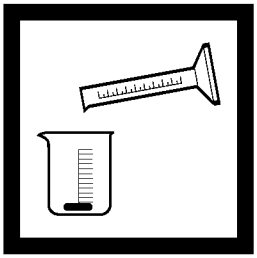
Phase 3: Titration of Sample for Total Residual Chlorine



1. Set-up the Amperometric Digital Titrator System as in *Phase 1: Adjusting the Electrode Response Slope* if it has not already been done. Reset the Digital Titrator counter to zero and wipe the tip.

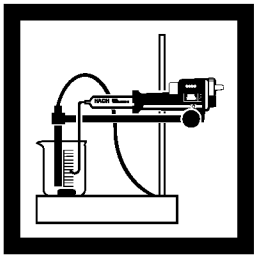
2. Place a clean 50-mm stirring bar supplied with the system into a clean 250-mL beaker. Using a Class A pipet, transfer 1.00 mL of 0.00564 N Sodium Thiosulfate Solution to the a beaker. Add 1 mL of pH 4 Acetate Buffer Solution to the beaker.

Note: *An improper size stirring bar can result in volatilization of chlorine, instability of readings and loss of sensitivity. Alternatively, use 0.00564 N Phenylarsine Oxide (PAO), Cat. No. 1999, instead of thiosulfate.*

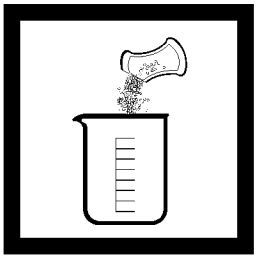


3. With minimum agitation, measure 200 mL sample with a clean graduated cylinder and transfer the sample to the beaker. Swirl to mix the reagents with sample.

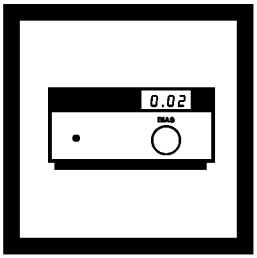
Note: *Steps 2-3 can be performed at the sampling site thereby "fixing" the sample for later analysis. Pipet 1.00 mL of 0.00564 N Sodium Thiosulfate and add 1.0 mL of Acetate Buffer into a clean, dry glass sampling bottle (e.g. BOD bottle). At the sample site, measure 200 mL of sample with a graduated cylinder and transfer to the sampling bottle. Swirl to mix. Before analysis, quantitatively transfer the entire contents of the sampling bottle to the 250-mL beaker. Minimize delay between sampling and analysis (1 hour maximum) to prevent decomposition of thiosulfate in the sample.*



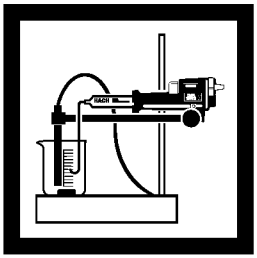
4. Place the beaker on the TitraStir Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



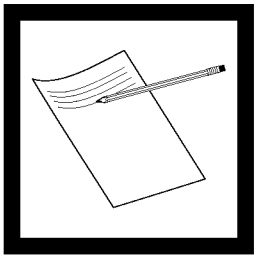
5. Add the contents of one pillow of Potassium Iodide Reagent to the beaker and allow the powder to dissolve.



6. Note the LED reading on the Amperometric Titrator. It should read 0.00 ± 0.05. DO NOT adjust the BIAS control.

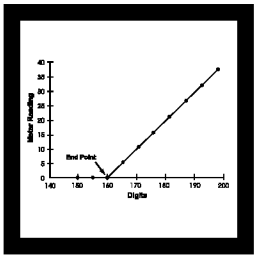


7. Using the Digital Titrator delivery knob, dispense the Standard Iodine Titrant Solution in 5-10 digit increments while noting the LED reading. Record at least 3 points (null current values and Digital Titrator reading), before end point is reached.

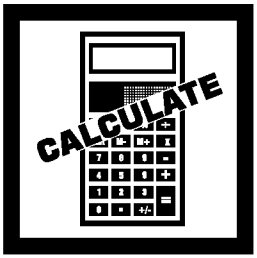


8. After the end point of the titration is reached, record the increasing LED readings along with the corresponding digits displayed on the Digital Titrator counter. Add 5-10 digits of titrant; wait a few seconds for a stable reading and record. Stop the titrant addition when the LED readings exceed 0.60.

Note: *LED readings above 0.60 will be excessively noisy. With samples containing excess de-chlorinating agents, such as sulfur dioxide, sulfite or bisulfite, the titration end point (number of digits) will be greater than the number of digits obtained during the standardization. It is not necessary to continue the titrant addition if the number of digits used in the sample titration exceeds that calculated for the standardization end point. This indicates that no free or combined chlorine is present in the sample.*



9. Using linear graph paper, plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the horizontal axis. Draw the two best intersecting lines through the points plotted. See *Figure 1* on page 90. Determine the number of digits at the intersection of the lines. This is the *sample* end point.



10. Calculate the µg/L total chlorine:

[Digits (Standard End Point) - Digits (Sample End Point)] x Multiplier = µg/L Cl_2
(Multiplier is from Phase 2.)

Example: Standard EP = 160 digits
Multiplier = 6.25
Sample EP = 150 digits

µg/L total chlorine =
[160 - 150] x 6.25 =
10 x 6.25 = 63 (round up)

Note: *To preserve the strength of the iodine titrant solution, always remove the delivery tube from the Digital Titrator cartridge and replace the cap when not in use. Protect the iodine titrant solution from direct sunlight.*

Table 1

Digits (standard end point)	Multiplier
160	6.25
165	6.06
170	5.88
175	5.71
180	5.56
185	5.40
190	5.26
195	5.13
200	5.00

Sampling and Storage

Chlorine is rapidly lost from water. Avoid exposure to sunlight or other strong light. Avoid excessive agitation. Analyze samples immediately or fix the sample by pre-addition of standard thiosulfate and buffer as indicated in *Phase 3: Titration of Sample for Total Residual Chlorine*. The fixing procedure should be used for brief transportation delays—not for storage of samples.

Accuracy Check

Standard Additions Method*

Snap the top off a Chlorine Standard Solution PourRite™ Ampule. Note the certificate value of the standard in mg/L.

1. Split a fresh sample into two 200-mL portions.

2. Using a TenSette® Pipet, add from 0.1 to 0.5 mL of the standard to one portion and swirl to mix. This is the *spiked sample*.

3. Analyze each sample as described above and record the chlorine concentrations.

4. Calculate the theoretical concentration of the spiked sample:

$$\text{heoretical concentration} = \frac{(C_u \times V_u) + (C_s \times V_s)}{V_u + V_s}$$

Where:

C_u = measured concentration of sample, in mg/L (µg/L divided by 1000)

V_u = volume of sample in mL

C_s = concentration of chlorine standard (mg/L, certificate value)

V_s = volume of standard added in mL

5. Calculate the percent spiked recovery:

$$\% \text{ Spike recovery} = \frac{\text{Spiked sample result, in mg/L}}{\text{Theoretical concentration calculated, in mg/L}} \times 100$$

* Standard additions is not applicable for samples containing excess reducing agents such as sulfur dioxide, sulfite, or bisulfite.

Example:

Sample result (C_u) = 120 µg/L or 0.120 mg/L

Spiked sample result = 185 µg/L or 0.185 mg/L

Volume Sample (V_u) = 200 mL

Volume Standard (V_s) = 0.2 mL

Chlorine Standard (C_s) = 68.1 mg/L

$$\text{heoretical concentration} = \frac{(0.120 \times 200) + (68.1 \times 0.2)}{200 + 0.2} = 0.188 \text{ mg/L}$$

Ideally, the percent recovery should be 100%. Generally, results from 80-120% recovery are considered acceptable.

Precision

In a single laboratory, using a standard solution of 120 µg/L chlorine, a single operator obtained a standard deviation of ± 19 µg/L chlorine.

Detection Limit

The estimated detectable concentration is equivalent to one digit of 0.0282 N Standard Iodine Titrant Solution or approximately 6 µg/L chlorine.

Interferences

- Silver ions poison the electrode.
- Copper ions interfere.
- Interferences are sometimes found in highly turbid water and those containing surface active agents.
- Oxidized manganese and other oxidizing reagents give positive interferences.
- Some uncertainty in the end point may be observed with samples containing high organic content.
- Iron and nitrite interference are minimized by buffering to pH 4 before adding potassium iodide.

- In samples containing excess reducing agents, such as sulfur dioxide, sulfite, and bisulfite, the titration end point will be shifted, indicating the sample contains no free or combined chlorine.

- Highly buffered samples or extreme sample pH may exceed the buffering capacity of the buffer reagent. If necessary, add additional buffer and check the pH of the sample prior to titration.

Summary of Method

The back titration procedure minimizes errors caused by liberating the full concentration of iodine in the sample and is the preferred method for amperometric measurement for total chlorine in wastewaters. In the back titration procedure, the end point signal is reversed because the remaining thiosulfate (or phenylarsine oxide) added to the sample is titrated with standard iodine. The end point of the back titration is reached just when free iodine exists in the sample resulting in a measurable polarization current. The end point is estimated by continued addition of titrant, recording of the current at each titrant addition, and graphing the data points. Where the best line between the data points intersects with the null current, the number of digits (from the Digital Titrator) at the end point can be determined and the concentration of chlorine calculated.

It is necessary to adjust the electrode sensitivity by using the bias control prior to performing the analysis. The bias adjustment is set by adding a known amount of standard iodine titrant to deionized water and adjusting the bias control to a given value on the display. The electrode sensitivity will vary depending on the probe conditioning. Adjustment should be made at least daily or before each series of samples.

Although the iodine titrant solution is formulated and packaged to be quite stable it is recommended the iodine be routinely standardized against standard thiosulfate or phenylarsine oxide. The number of digits determined for the iodine standardization is recorded and used in the calculation of the sample's chlorine concentration.

To preserve the strength of the iodine titrant solution, always remove the delivery tube from the Digital Titrator cartridge and replace the cap when not in use. Protect the iodine titrant solution from direct sunlight.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Acetate Buffer Solution, pH 4.0	100 mL MDB	14909-32
Potassium Iodide Powder Pillows	100/pkg	1077-99
Standard Iodine Titrant Solution, 0.028 N	each	23333-01
Sodium Thiosulfate Standard Solution, 0.00564 N	100 mL	24088-42

REQUIRED APPARATUS

Amperometric Titrator Assembly	each	19299-00
Beaker, low-form, 250-mL	each	500-46
Cylinder, graduated, 250-mL	each	508-46
Digital Titrator	each	16900-01
Delivery Tubes, 90° with hook	5/pkg	41578-00
Pipet, volumetric, Class A, 1-mL	each	14515-35
Probe Assembly, Amperometric Titrator	each	19390-00
Stir Bar, octagonal, Teflon-coated, 50.8 x 7.9 mm	each	20953-55
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

OPTIONAL REAGENTS

Chlorine Standard Solution PourRite™ Ampules, 50-75 mg/L Cl_2, 2-mL	20/pkg	14268-20
Phenylarsine Oxide Solution, 0.00564 N	100 mL	1999-42
Water, deionized	4 L	272-56

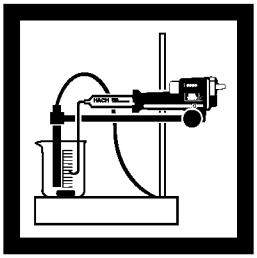
OPTIONAL APPARATUS

Bottle, BOD, 300-mL	each	621-00
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
PourRite™ Ampule Breaker	each	24846-00

CHLORINE, TOTAL (0 to 1000 µg/L as Cl_2) For drinking water or wastewater

Amperometric Forward Titration

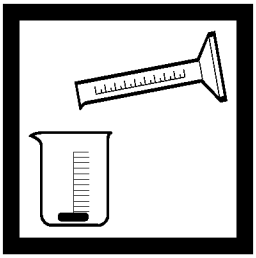
USEPA Accepted for Reporting*



1. Assemble the Amperometric Digital Titrator System according to the instructions in the *Amperometric Titrator Instruction Manual*.

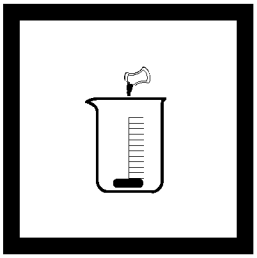
2. Install the Phenylarsine Oxide (PAO), 0.00564 N Cartridge. Flush the Digital Titrator delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *When a new probe is used or when the probe has not been used recently, prepare it according to the Probe Stabilization instructions in the Amperometric Titrator Instruction Manual.*



3. With minimum agitation, measure 200 mL sample with a clean graduated cylinder. Transfer the sample to a clean 250-mL beaker containing the 50-mm stirring bar supplied with the system.

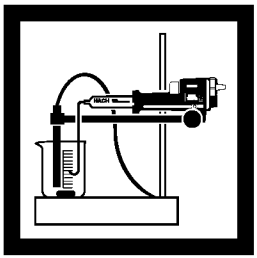
Note: *An improper size of stirring bar can result in volatilization of chlorine, instability of readings and loss of sensitivity.*



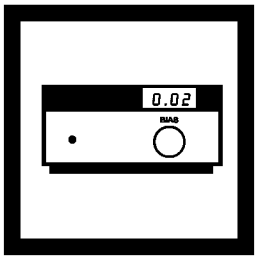
4. Add the contents of one Potassium Iodide Powder Pillow and swirl to dissolve.

* Procedure is equivalent to USEPA method 330.1 and 330.3, *Standard Methods for the Examination of Water and Wastewater* (18th ed.) 4500-Cl D for drinking water and *Standard Methods* (17th ed.) 4500-Cl D for wastewater.

5. Add 1 mL of pH 4 Acetate Buffer Solution.

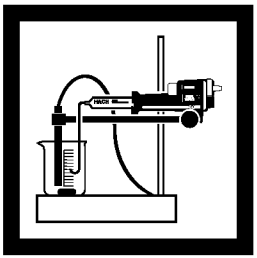


6. Place the beaker on the TitraStir® Stir Plate and immerse the tips of the probe and delivery tube in the solution. The probe's platinum wires must be submerged. Turn on the stirring motor.



7. Note the LED reading on the Amperometric Titrator. Unlock the BIAS control and adjust the BIAS control knob until a reading between 0.50-0.60 is obtained. Lock the BIAS control.

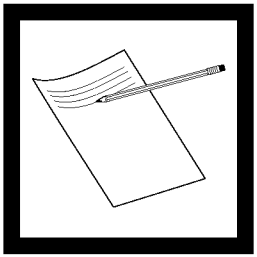
Note: *The bias adjustment controls the slope of the titration curve. The actual instrument reading is not important; but rather the change in the readings as the titration proceeds. The adjustment need not be precise.*



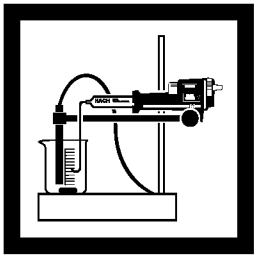
8. Using the Digital Titrator delivery knob, dispense the PAO titrant Solution in 5-10 digit increments while noting the downward reading.

Note: *If the chlorine content of the sample is high, add titrant at a faster rate; only the end point of the titration and the volume of titrant used at the end point are of concern. For example, if the chlorine content is approximately 500 µg/L, up to 300 digits of 0.00564 N PAO could be added at once. As the end point is approached, dispense in small increments.*

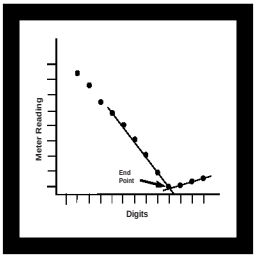
Note: *If excess reductant, such as sulfite, bisulfite, or sulfur dioxide is present in the sample, the LED readings will not decrease and may even increase. This indicates that no free chlorine or chloramines are present in the sample.*



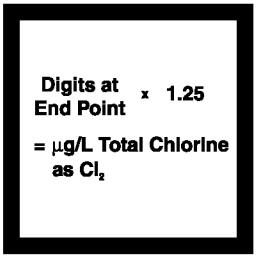
9. As the end point of the titration is approached, record the LED readings along with the corresponding digits displayed on the Digital Titrator counter. Near the titration end point, add 2 to 5 digits of titrant; wait a few seconds for a stable reading and record.



10. Continue the titration, recording at least three points on the downward sloping curve and at least three points after the end point has been reached. The latter points will have little change in the LED readings.



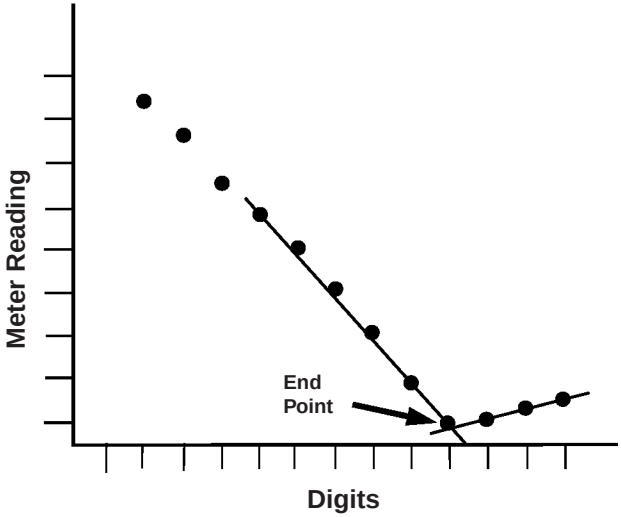
11. Using linear graph paper, plot the recorded readings from the Amperometric Titrator on the vertical axis and the corresponding Digital Titrator digits on the the on the horizontal axis. Draw the two best intersecting lines through the points see *Figure 1*. Determine the number of digits at the intersection of the lines; this is the end point.



12. Calculate the µg/L total chlorine:

Digits at End Point X 1.25 = µg/L total chlorine as Cl_2

Figure 1
Sample Plot



Accuracy Check

Standard Additions Method*

1. Snap the top off a Chlorine Standard Solution PourRite™ Ampule. Note the certificate value of the standard in mg/L.
2. Split a fresh sample into two 200-mL portions.
3. Using a TenSette® Pipet, add from 0.1 to 0.5 mL of the standard to one portion and swirl to mix. This is the *spiked sample*.
4. Analyze both the sample and spiked sample and record the concentration of each.
5. Calculate the theoretical concentration of the spiked sample:

$$\text{heoretical concentration} = \frac{(C_u \times V_u) + (C_s \times V_s)}{V_u + V_s}$$

Where:

C_u = measured concentration of sample, in mg/L (µg/L divided by 1000)

V_u = volume of sample in mL

C_s = concentration of chlorine standard (mg/L, certificate value)

V_s = volume of standard added in mL

6. Calculate the percent spiked recovery:

$$\text{Spike Recovery} = \frac{\text{Spiked sample result, in mg/L}}{\text{Theoretical concentration calculated, in mg/L}} \times 100$$

Example:

Sample result (C_u) = 120 µg/L or 0.120 mg/L

Spiked sample result = 185 µg/L or 0.185 mg/L

Volume Sample (V_u) = 200 mL

Volume Standard (V_s) = 0.2 mL

Chlorine Standard (C_s) = 68.1 mg/L

* The standard additions technique is not applicable for samples containing excess reducing agents such as sulfur dioxide, sulfite, or bisulfite.

$$\text{heoretical concentration} = \frac{(0.120 \times 200) + (68.1 \times 0.2)}{200 + 0.2} = 0.188 \text{ mg/L}$$

Ideally, the percent recovery should be 100%. Generally, results from 80-120% recovery are considered acceptable.

Precision

In a single laboratory, using a standard solution of 347 µg/L chlorine, a single operator obtained a standard deviation of ± 3.2 µg/L chlorine.

Detection Limit

With good operator technique, the estimated detectable concentration is approximately 15 µg/L chlorine using 0.00564 N PAO.

Sampling and Storage

Chlorine is rapidly lost from water. Avoid exposure to sunlight or other strong light. Avoid excessive agitation. Analyze samples immediately.

Interferences

- Silver ions poison the electrode.
- Copper ions interfere.
- Interferences are sometimes found in highly turbid water and those containing surface active agents. Oxidized manganese and other oxidizing reagents give positive interferences.
- Some uncertainty in the end point may be observed with samples containing high organic content.
- Samples containing excess reducing agents, such as sulfur dioxide, sulfite, and bisulfite, do not contain free chlorine or chloramines and can not be titrated under the conditions of the test.
- Highly buffered samples or extreme sample pH may exceed the buffering capacity of the buffer reagent. If necessary, add additional buffer and check pH of sample prior to titration.

Summary of Method

In the amperometric forward titration procedure for total chlorine, a small electrical current is applied across two identical platinum electrodes. No current can flow between the electrodes unless a substance that can be oxidized at the anode and a substance that can be reduced at the cathode are both present. In the case of the total chlorine, an equivalent amount of iodine forms from the reaction of excess iodide with chlorine and combined chlorine at pH 4. During the titration with phenylarsine oxide (PAO), the free iodine is reduced to iodide at the cathode and PAO is oxidized from the +3 oxidation state to the +5 oxidation state at the anode. Prior to the end point of the titration, both iodine and iodide are present in solution; therefore current can flow, even with a very small applied potential. At the end point, no free iodine remains and the solution cannot conduct even if excess PAO titrant is added. The end point is defined when no change in current occurs, signaling all total chlorine has been reacted.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Phenylarsine Oxide Solution 0.00564 N Digital Titrator cartridge	each	1999-01
Acetate Buffer Solution, pH 4	100 mL MBD	14909-32
Potassium Iodide Powder Pillows	100/pkg	1077-99

REQUIRED APPARATUS

Amperometric Titrator Assembly	each	19299-00
Digital Titrator	each	16900-01
Beaker, low-form, 250-mL	each	500-46
Cylinder, graduated, 250-mL	each	508-46
Delivery Tubes, 90° with hook	5/pkg	41578-00
Probe Assembly, Amperometric Titrator	each	19390-00
Stir Bar, octagonal, Teflon-coated, 50.8 x 7.9 mm	each	20953-55
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

OPTIONAL REAGENTS

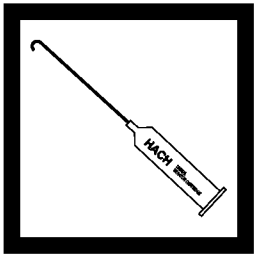
Chlorine Standard Solution PourRite™ Ampules, 50-75 mg/L Cl_2, 2-mL	20/pkg	14268-20
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

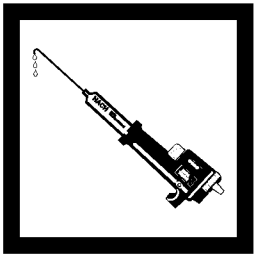
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
PourRite™ Ampule Breaker	each	24846-00
Standard Methods for the Examination of Water and Wastewater, 19th edition	each	22708-00

CHROMATE (20 to > 400 mg/L as CrO_4^{2-})

Using Sodium Thiosulfate

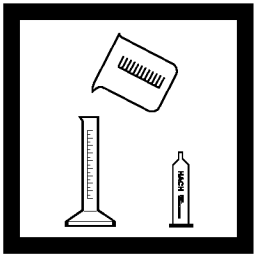


1. Insert a clean delivery tube into the Sodium Thiosulfate titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



2. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

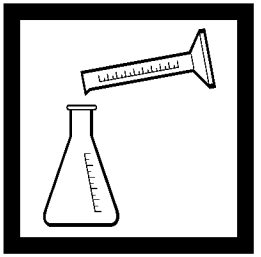
Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



3. Select a sample volume corresponding to the expected chromate (CrO_4^{2-}) concentration from *Table 1*.

Note: *Collect 200 to 300 mL of sample in an acid-washed glass or polyethylene container.*

Note: *See Sampling and Storage following these steps.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample to a clean 125-mL Erlenmeyer flask. Dilute to about the 50-mL mark with deionized water.

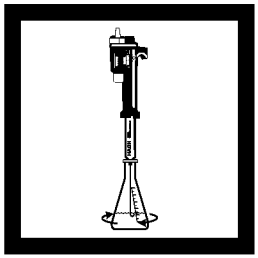
Table 1

Range (mg/L as CrO_4^{2-})	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
20-80	50	0.2068 N	22676-01	0.2
50-200	20	0.2068 N	22676-01	0.5
100-400	10	0.2068 N	22676-01	1.0
> 400	5	0.2068 N	22676-01	2.0

5. Add the contents of one Potassium Iodide Powder Pillow and swirl to mix.

6. Add the contents of one Dissolved Oxygen 3 Reagent Powder Pillow and swirl to mix. Wait at least three minutes but not more than 10 minutes before completing *steps 7 to 9.*

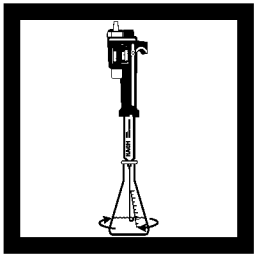
Note: *A yellow or brown color indicates the presence of chromate.*



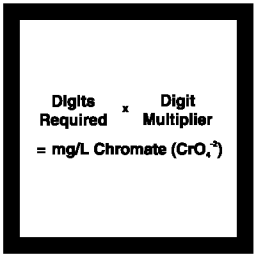
7. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate to a straw-yellow color.

8. Add one dropper of Starch Indicator Solution and swirl to mix.

Note: *A blue color will form.*



9. Continue titrating until the solution turns from blue to colorless. Record the number of digits required.



10. Calculate:

Total Digits Required x Digit Multiplier = mg/L chromate (CrO_4^{2-})

Note: *Results may be expressed as mg/L sodium chromate (Na_2CrO_4) or chromium (Cr) by multiplying the mg/L chromate by 1.4 or 0.448, respectively.*

Sampling and Storage

Collect 200 to 300 mL of sample in an acid-washed glass or polyethylene container. If sample cannot be analyzed immediately add 1 mL concentrated sulfuric acid and swirl to mix.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Use a TenSette® Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of Hexavalent Chromium Standard Solution, 1000 mg/L to three samples of the same volume as that titrated in the procedure.

2. Analyze each as described in the procedure.

3. Each 0.1 mL addition of standard should require 22 additional digits of titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Standard Preparation

A standard solution equivalent to 67 mg/L chromate (30 mg/L Cr) can be prepared by diluting 3.0 mL of Hexavalent Chromium Standard Solution, 1000 mg/L Cr to 100 mL in a volumetric flask. Titrate a 20-mL or 50-mL sample as described in the procedure.

Interferences

Substances capable of oxidizing iodide to iodine under acidic conditions (such as ferric iron and copper) will interfere to give high results. The effects of iron and copper may be masked by dissolving a Magnesium CDTA Powder Pillow, followed by two 1.0-gram measuring spoons of Sodium Acetate in the sample between *steps 6 and 7*.

Summary of Method

Chromate in the sample reacts with iodide under acidic conditions to form iodine as triiodide. Addition of starch indicator produces a blue color complex with the iodine. This complex is titrated with sodium thiosulfate to a colorless end point. The volume of titrant used is proportional to the chromate concentration.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Chromate Reagent Set (about 100 tests)		22724-00
Includes: (1) 349-32, (1) 987-99, (1) 20599-96, (1) 22676-01		
Dissolved Oxygen 3 Reagent Powder Pillows	100/pkg	987-99
Potassium Iodide Powder Pillows	50/pkg	20599-96
Sodium Thiosulfate Titration Cartridge, 0.2068 N	each	22676-01
Starch Indicator Solution	100 mL MDB	349-32
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125-mL	each	505-43
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41

OPTIONAL REAGENTS

Chromium, Hexavalent, Standard Solution, 1000 mg/L	100 mL	14664-42
Magnesium CDTA Powder Pillows	100/pkg	14080-99
Sodium Acetate, trihydrate, ACS	100 g	178-26

OPTIONAL APPARATUS

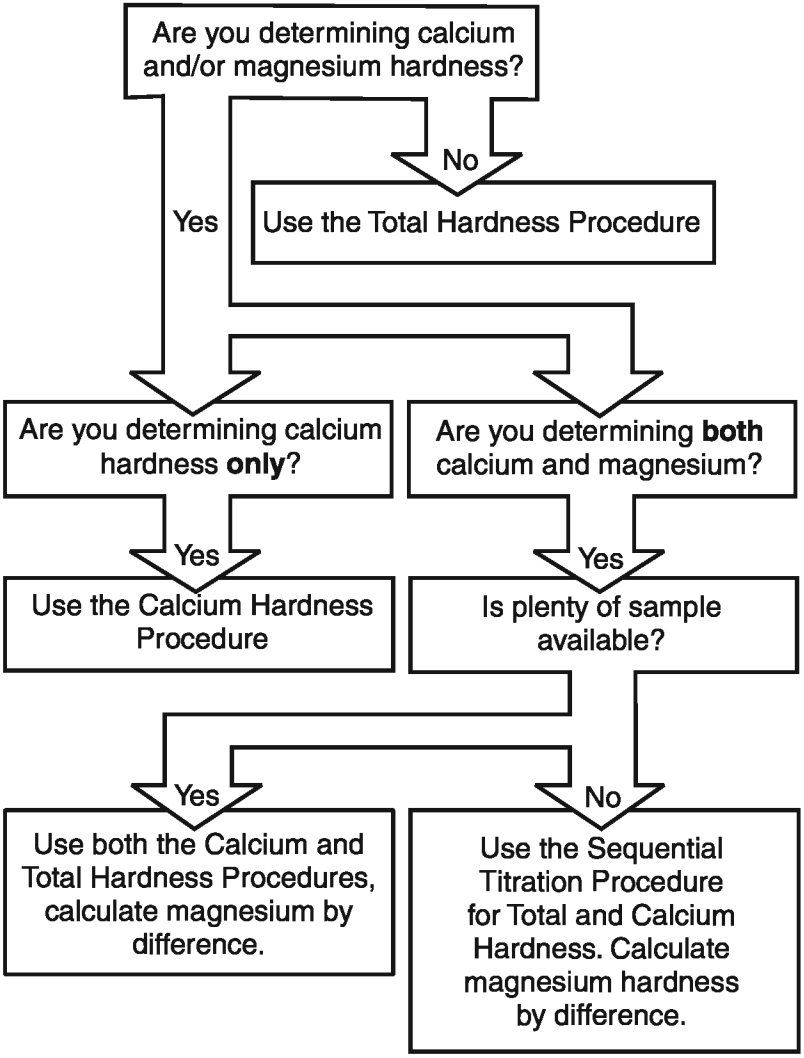
Clamp, 2-prong, extension	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Flask, volumetric, Class B, 100 mL	each	547-42
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01

OPTIONAL APPARATUS, continued

Description	Unit	Cat. No.
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 3-mL	each	14515-03
Pipet, volumetric, Class A, 5-mL	each	14515-37
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet Filler, safety bulb	each	14651-00
Spoon, measuring, 1.0-gram	each	510-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

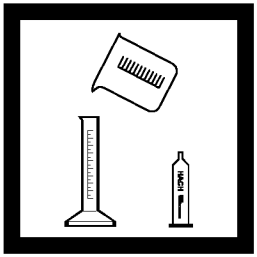
HARDNESS DECISION TREE

There are several hardness procedures presented in this manual. Use the following decision tree to select the appropriate procedure for your application.



HARDNESS, CALCIUM (10 to 4000 mg/L as $CaCO_3$)

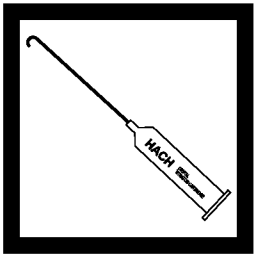
Using EDTA



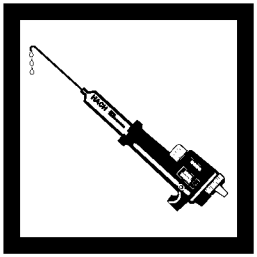
1. Select a sample size and an EDTA Titration Cartridge corresponding to the expected calcium as calcium carbonate ($CaCO_3$) concentration. Use *Table 1* for concentrations in mg/L or *Table 2* for concentrations in German degrees of hardness (G.d.h.).

Note: *One German degree hardness equals 17.9 mg/L hardness as $CaCO_3$.*

Note: *If sample cannot be analyzed immediately, add 1.5 mL Nitric Acid per liter of sample to preserve the sample and to prevent adsorption of the calcium to the container walls. Store in a refrigerator. Samples preserved in this manner are stable for one week. Neutralize to pH 7 before running the test.*

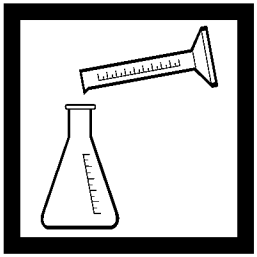


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1* or *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

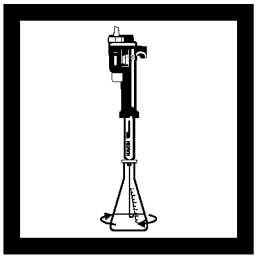
5. Add 2 mL of 8 N Potassium Hydroxide Standard Solution and swirl to mix.

Note: *For samples of 50 mL or less, 1 mL may be added.*

Note: *Magnesium is not included in the results but must be present for a sharp end point. If it is known to be absent, add one to two drops of Magnesium Standard Solution, 10 g/L as $CaCO_3$.*

6. Add the contents of one CalVer® 2 Calcium Indicator Powder Pillow (Cat. No. 852-99) and swirl to mix.

Note: *A 0.1-gram scoop of CalVer 2 Calcium Indicator Powder (Cat. No. 281-14) may be substituted here.*



7. Place the delivery tube tip into the solution and swirl the flask while titrating with EDTA from pink to blue. Record the number of digits required.

Note: *Titrate slowly near the end point, because the reaction is slow, especially in cold samples.*

8. Calculate the sample concentration using one of the formulas below:

Total Digits Required x Digit Multiplier (*Table 1*) = mg/L Calcium Hardness as $CaCO_3$

Total Digits Required x Digit Multiplier (*Table 2*) = G.d.h.

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
10-40	100	0.0800	14364-01	0.1
40-160	25	0.0800	14364-01	0.4
100-400	100	0.800	14399-01	1.0
200-800	50	0.800	14399-01	2.0
500-2000	20	0.800	14399-01	5.0
1000-4000	10	0.800	14399-01	10.0

Table 2

Range (G.d.h.)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
1-4	100	0.1428	14960-01	0.01
4-16	25	0.1428	14960-01	0.04
10-40	50	0.714	14959-01	0.1
25-100	20	0.714	14959-01	0.25
>100	10	0.714	14959-01	0.5

Hardness Relationships

mg/L Ca = Ca Hardness, mg/L as $CaCO_3$ x 0.40

Accuracy Check

Standard Additions Method
This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Hardness Standard Solution Voluette® Ampule, 10,000 mg/L as $CaCO_3$.
2. Use a TenSette® Pipet to add 0.1 mL of standard to the solution titrated in *step 7*. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 10 additional digits of 0.800 N titrant or 100 digits of 0.0800 N titrant (11 digits of 0.714 M or 56 digits of 0.1428 M titrant). If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

WARNING:
Potassium cyanide is toxic. Always add it after the potassium hydroxide. Excess potassium cyanide does not affect results. All cyanide wastes should be disposed of by adding an excess of strongly alkaline sodium hypochlorite solution (bleach) with stirring. Use good ventilation. Allow to stand for 24 hours before disposal.

- Some transition and heavy metals complex the indicators and prevent the color change at the end point. Adding a 0.5-g scoop of potassium cyanide (KCN) after the addition of potassium hydroxide removes interference from the following metals at the levels listed (in an undiluted 100-mL sample), see *Table 3*.

Table 3

Metal	Max. Tolerance Level* with KCN	Max. Tolerance Level* without KCN present
Cobalt	20 mg/L	none
Copper	100 mg/L	0.10 mg/L
Nickel	200 mg/L	0.5 mg/L
Zinc	100 mg/L	5 mg/L

* Proportionally higher levels of these elements are tolerable in smaller sample sizes since their effect is diluted when bringing the volume to 100 mL. Because Tables 1 and 2 have sample volumes of 10-100 mL, the interference concentrations may be greater in your sample and have no effect because of sample dilution.

- Iron interferes above 8 mg/L in undiluted samples. Above this level, it causes a red-orange to green end point which is sharp and usable up to 20 mg/L iron.
- Manganese interferes above 5 mg/L.
- Aluminum causes a slow end point, but up to 200 mg/L can be tolerated by allowing enough time for color change.
- Magnesium interference up to 200 mg/L is prevented by formation of magnesium hydroxide at the high test pH, but higher levels prevent a distinct end point.
- Orthophosphate causes a slow end point, but does not interfere if the calcium phosphate that forms is allowed enough time to redissolve during the titration. Polyphosphate must be absent for accurate results.
- Barium and strontium are titrated with calcium but seldom present in natural waters in significant amounts.
- Acidity and alkalinity at 10,000 mg/L as $CaCO_3$ do not interfere.
- Saturated sodium chloride solutions do not give a distinct end point, but the titration can be run directly on sea water.

- Samples at about 20 °C (68 °F) or colder should be titrated slowly near the end point to allow enough time for the color change.
- Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.

Summary of Method

The sample is made alkaline (pH 12-13) with potassium hydroxide to precipitate magnesium as magnesium hydroxide. CalVer 2 Indicator is added and combines with any calcium to form a pink-red color. As EDTA is added, it reacts with the free calcium ions present. When no free calcium ions remain, the EDTA then removes the calcium complexed with the indicator, causing a color change to blue.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Calcium Hardness Reagent Sets (about 100 tests)		
1-16 G.d.h. includes: (1) 282-32, (1) 852-99, (1) 14960-01		24473-00
10-100+ G.d.h. includes: (1) 282-32, (1) 852-99, (1) 14959-01		24474-00
10-160 mg/L includes: (1) 282-32, (1) 852-99, (1) 14364-01		24472-00
100-4,000 mg/L includes: (1) 282-32, (1) 852-99, (1) 14399-01		24475-00
CalVer® 2 Indicator Powder Pillows	100/pkg	852-99
Potassium Hydroxide Standard Solution, 8.00 N	100 mL MDB*	282-32
Water, deionized	4 L	272-56
Select one or more based on sample concentration:		
EDTA Titration Cartridge, 0.0800 M	each	14364-01
EDTA Titration Cartridge, 0.1428 M	each	14960-01
EDTA Titration Cartridge, 0.714 M	each	14959-01
EDTA Titration Cartridge, 0.800 M	each	14399-01

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250 mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, 100 mL	each	508-42

* Marked Dropper Bottle (MDB). Contact Hach for larger sizes.

OPTIONAL REAGENTS

Calcium and Magnesium Total Hardness Reagent Set (about 100 tests) 22721-00
Includes: (2) 282-32, (1) 424-32, (1) 851-99, (1) 947-99, (1) 14364-01, (1) 14399-01

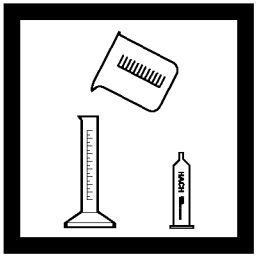
Description	Unit	Cat. No.
Calcium Chloride Standard Solution, 1000 mg/L as $CaCO_3$	1000 mL	121-53
CalVer® 2 Calcium Indicator Powder	113 g	281-14
Calcium Standard Solution Voluette® Ampules, 10,000 mg/L as $CaCO_3$, 10-mL	16/pkg	2187-10
Magnesium Standard Solution, 10 g/L $CaCO_3$	29 mL SCDB	1022-33
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Potassium Cyanide, ACS	125 g	767-14

OPTIONAL APPARATUS

Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong, extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
pH Paper, 1.0 to 11 pH	5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion**™1* Basic Portable pH Meter with electrode	each	51700-10
Spoon, measuring, 0.1-gram	each	511-00
Spoon, measuring, 0.5-gram	each	907-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

HARDNESS, TOTAL (10 to 4000 mg/L as $CaCO_3$)

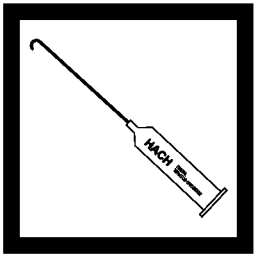
Using EDTA



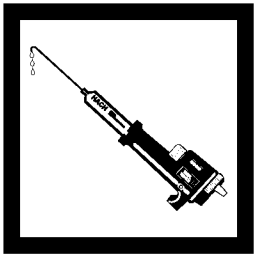
1. Select a sample size and an EDTA Titration Cartridge corresponding to the expected total hardness as calcium carbonate ($CaCO_3$) concentration. Use *Table 1* for concentrations in mg/L or *Table 2* for concentrations in German degrees of hardness (G.d.h.).

Note: *One German degree hardness equals 17.9 mg/L hardness as $CaCO_3$.*

Note: *Collect at least 100 mL of sample in a glass or polyethylene container. Samples may be held up to seven days before analysis if stored at 4 °C and acidified to pH 2 with concentrated nitric acid. Neutralize acidified sample to pH 7 with ammonium hydroxide before testing.*

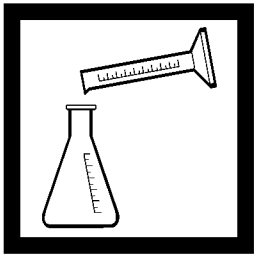


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

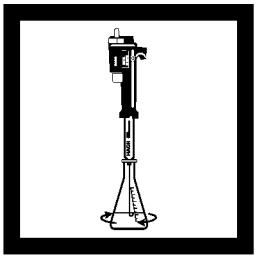


4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1* or *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

5. Add 2 mL of Hardness 1 Buffer Solution and swirl to mix.

6. Add the contents of one ManVer® 2 Hardness Indicator Powder Pillow (Cat. No. 851-99) and swirl to mix.

Note: *Four drops of ManVer Hardness Indicator Solution or a 0.1 g scoop of ManVer 2 Hardness Indicator Powder (Cat. No. 280-14) may be substituted for the powder pillow.*



7. Place the delivery tube tip into the solution and swirl the flask while titrating with EDTA from red to pure blue. Record the number of digits required.

Note: *Titrate slowly near the end point because the reaction is slow, especially in cold samples.*

8. Use one of the following formulas to calculate the final concentration:

Digits Required x Digit Multiplier (*Table 1*) = mg/L Total Hardness as $CaCO_3$

Digits Required x Digit Multiplier (*Table 2*) = G.d.h.

Note: *The magnesium concentration may be determined by subtracting the results of the calcium determination from total hardness.*

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
10-40	100	0.0800	14364-01	0.1
40-160	25	0.0800	14364-01	0.4
100-400	100	0.800	14399-01	1.0
200-800	50	0.800	14399-01	2.0
500-2000	20	0.800	14399-01	5.0
1000-4000	10	0.800	14399-01	10.0

Table 2

Range (G.d.h.)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
1-4	100	0.1428	14960-01	0.01
4-16	25	0.1428	14960-01	0.04
10-40	50	0.714	14959-01	0.1
25-100	20	0.714	14959-01	0.25
>100	10	0.714	14959-01	0.5

Hardness Relationships

$$\text{g/L Total Hardness as Ca} = \text{mg/L Total Hardness as } (CaCO_3) \times 0.400$$

$$\text{mg/L Total Hardness (as } CaCO_3) = \text{mg/L Ca (as } CaCO_3) + \text{mg/L Mg (as } CaCO_3)$$

Accuracy Check

Standard Additions Method
To verify analytical technique, use 20 mL of the Calcium Standard Solution, 1000 mg/L as $CaCO_3$. Perform the procedure as described above. This solution will read 1000 mg/L or 55.9 G.d.h.

Perform this accuracy check when interferences are suspected.

1. Snap the neck off a Hardness Standard Solution Voluette® Ampule, 10,000 mg/L as $CaCO_3$.

2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in *step 7*. Resume titration back to the same end point. Record the number of digits required.

3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.

4. Each 0.1 mL addition of standard should require 10 additional digits of 0.800 M titrant, 100 digits of 0.0800 M titrant, 11 digits of 0.714 M, or 56 digits of 0.1428 M titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- Although less common than calcium and magnesium, other polyvalent metal ions cause the same hardness effects and will be included in the results.
- Some transition and heavy metals complex the indicator and prevent the color change at the end point.
- Iron does not interfere up to 15 mg/L. Above this level it causes a red-orange to green end point which is sharp and

usable up to 30 mg/L iron. Substitute a 0.0800 M CDTA or 0.800 M CDTA titration cartridge for the 0.0800 M EDTA or 0.800 M EDTA titration cartridges, respectively, if iron interference is probable.

- Manganese titrates directly up to 20 mg/L but masks the end point above this level. Adding a 0.1-gram scoop of hydroxylamine hydrochloride monohydrate raises this level to 200 mg/L manganese.

WARNING
Potassium cyanide is toxic. Always add it after the potassium hydroxide. Excess potassium cyanide does not affect results. All cyanide wastes should be disposed of by adding an excess of strongly alkaline sodium hypochlorite solution (bleach) with stirring. Use good ventilation. Allow to stand for 24 hours before disposal.

- Copper and aluminum interfere at levels above 0.10 and 0.20 mg/L, respectively. Cobalt and nickel interfere at all levels and must be absent or masked. A 0.5-gram scoop of potassium cyanide removes interference from up to 100 mg/L copper, 100 mg/L zinc, 100 mg/L cobalt, and 100 mg/L nickel. It raises the permissible aluminum level to 1 mg/L. Metals masked with cyanide will not be included in the hardness result.
- Orthophosphate causes a slow end point and polyphosphate must be absent for accurate results.
- Acidity and alkalinity at 10,000 mg/L (as $CaCO_3$) do not interfere.
- Saturated sodium chloride solutions do not give a distinct end point, but the titration can be run directly on sea water.
- Adding the contents of one CDTA Magnesium Salt Powder Pillow removes metal interferences at or below the levels shown in *Table 3*.

Table 3

Metal	CDTA Removes Interference Below This Level
Aluminum	50 mg/L
Cobalt	200 mg/L
Copper	100 mg/L
Iron	100 mg/L
Manganese	200 mg/L
Nickel	400 mg/L
Zinc	300 mg/L

- If more than one metal is present at or above the concentrations shown above, an additional CDTA Magnesium Salt Powder Pillow may be required.

Results obtained by this procedure include the hardness contributed by the metals. If the concentration of each metal is known, a correction can be applied to obtain the calcium and magnesium hardness concentration. The hardness (in mg/L as $CaCO_3$) contributed by each mg/L of metal is listed below, and can be subtracted from the total hardness value obtained above to determine the calcium and magnesium hardness. See *Table 4*.

Table 4

Metal	Hardness as $CaCO_3$ Contributed by Each mg/L of Metal
Aluminum	3.710
Barium	0.729
Cobalt	1.698
Copper	1.575
Iron	1.792
Manganese	1.822
Nickel	1.705
Strontium	1.142
Zinc	1.531

- Barium, strontium and zinc titrate directly.
- Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.

Summary of Method

After the sample is buffered to pH 10.1, ManVer 2 Hardness Indicator is added, and forms a red complex with a portion of the calcium and magnesium in the sample. EDTA titrant reacts first with the free calcium and magnesium ions, then with those bound to the indicator, causing it to change to a blue color at the end point.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Total Hardness Reagent Sets (about 100 tests)		
1-16 G.d.h. includes: (1) 424-32, (1) 851-99, (1) 14960-01		24478-00
10-100+ G.d.h. includes: (1) 424-32, (1) 851-99, (1) 14959-01		24479-00
10-160 mg/L includes: (1) 424-32, (1) 851-99, (1) 14364-01		24480-00
100-4,000 mg/L includes: (1) 424-32, (1) 851-99, (1) 14399-01		24481-00
Hardness 1 Buffer Solution	100 mL MDB	424-32
ManVer® 2 Hardness Indicator Powder Pillow	100/pkg	851-99
Water, deionized	4 L	272-56
Select one or more based on sample concentration:		
EDTA Titration Cartridge, 0.0800 M	each	14364-01
EDTA Titration Cartridge, 0.1428 M	each	14960-01
EDTA Titration Cartridge, 0.714 M	each	14959-01
EDTA Titration Cartridge, 0.800 M	each	14399-01

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Ammonium Hydroxide, 10%	100 mL MDB*	14736-32
Calcium Chloride Standard Solution, 1000 mg/L as $CaCO_3$	1000 mL	121-53
CDTA Magnesium Salt Powder Pillows	100/pkg	14080-99
CDTA Titration Cartridge, 0.0800 M	each	14402-01
CDTA Titration Cartridge, 0.800 M	each	14403-01
Calcium Standard Solution Voluette® Ampules, 10,000 mg/L as $CaCO_3$, 10-mL	16/pkg	2187-10
Hydroxylamine Hydrochloride, Monohydrate, ACS	113 g	246-14
ManVer® 2 Hardness Indicator Powder	113 g	280-14
ManVer® Hardness Indicator Solution	100 mL MDB*	425-32
Nitric Acid Solution, 1:1	500 mL	2540-49
Nitric Acid, ACS	500 mL	152-49
Potassium Cyanide, ACS	125 g	767-14

* Contact Hach for larger sizes.

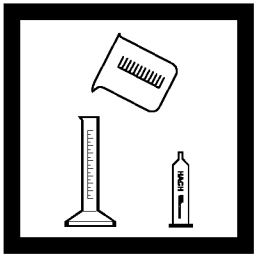
OPTIONAL APPARATUS

Description	Unit	Cat. No.
Bottle, wash, poly, 500-mL	each	620-11
Clamp 2-prong, extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
pH Paper, 1.0 to 11 pH	5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion***™*1* Basic Portable pH Meter with electrode	each	51700-10
Spoon, measuring, 0.1-gram	each	511-00
Spoon, measuring, 0.5-gram	each	907-00
Spoon, measuring, 1.0-gram	each	510-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

HARDNESS, TOTAL, SEQUENTIAL (10 to 4000 mg/L as $CaCO_3$)

Sequential Titration Procedure (Limited Sample)

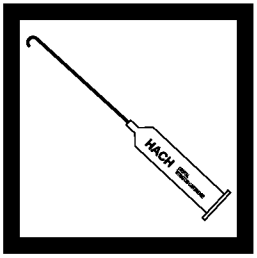
Scope and Application: To determine total and calcium hardness in samples with limited sample size, follow this procedure. Calculate magnesium hardness by difference.



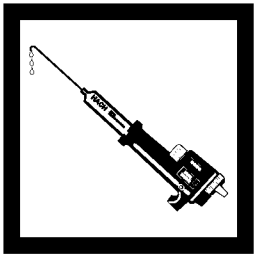
1. Select a sample size and an EDTA Titration Cartridge corresponding to the expected calcium as calcium carbonate ($CaCO_3$) concentration. Use *Table 1* for concentrations in mg/L or *Table 2* for concentrations in German degrees of hardness (G.d.h.).

Note: *One German degree hardness equals 17.9 mg/L hardness as $CaCO_3$.*

Note: *If sample cannot be analyzed immediately, add 1.5 mL Nitric Acid per liter of sample to preserve the sample and to prevent adsorption of the calcium to the container walls. Store in a refrigerator. Samples preserved in this manner are stable for one week. Neutralize to pH 7 before running the test.*

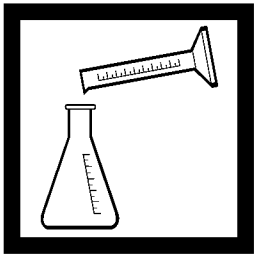


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience, use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1* or *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

Table 1

Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
10-40	100	0.0800	14364-01	0.1
40-160	25	0.0800	14364-01	0.4
100-400	100	0.800	14399-01	1.0
200-800	50	0.800	14399-01	2.0
500-2000	20	0.800	14399-01	5.0
1000-4000	10	0.800	14399-01	10.0

Table 2

Range (G.d.h.)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
1-4	100	0.1428	14960-01	0.01
4-16	25	0.1428	14960-01	0.04
10-40	50	0.714	14959-01	0.1
25-100	20	0.714	14959-01	0.25
>100	10	0.714	14959-01	0.5

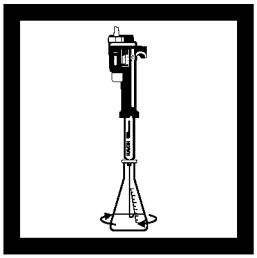
5. Add 2 mL of 8 N Potassium Hydroxide Standard Solution and swirl to mix.

Note: *For samples of 50 mL or less, 1 mL may be added.*

Note: *Magnesium is not included in the results but must be present for a sharp end point. If it is known to be absent, add 1–2 drops of Hardness Standard Solution.*

6. Add the contents of one CalVer® 2 Calcium Indicator Powder Pillow (Cat. No. 947-99) and swirl to mix.

Note: *Do not use potassium cyanide to eliminate interferences or toxic gas will form in subsequent steps.*



7. Place the delivery tube tip into the solution and swirl the flask while titrating with EDTA from pink to blue. Record the number of digits required.

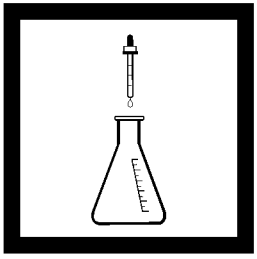
Note: *Titrate slowly near the end point, because the reaction is slow, especially in colder samples.*

8. Calculate the sample concentration of calcium hardness by using one of the formulas below:

Digits Required x Digit Multiplier (*Table 1*) = mg/L Calcium Hardness as CaCO3

Digits Required x Digit Multiplier (*Table 2*) = G.d.h.

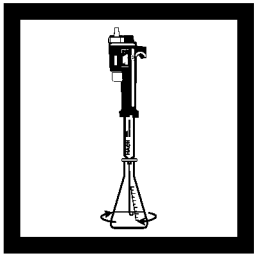
Note: *Do not reset the counter to zero.*



9. After completing the calcium titration, add 1 mL of 5.25 N Sulfuric Acid Standard Solution. Add additional acid dropwise and swirl the solution until the color changes from pure blue to purple, then to blue and finally to red. Swirl the flask to ensure that all precipitated magnesium hydroxide has redissolved.

10. Add 2 mL of Hardness 1 Buffer Solution and swirl to mix.

11. Add the contents of one ManVer® 2 Hardness Indicator Powder Pillow (Cat. No. 928-99) or 4 drops of Hardness 2 Test Solution (Cat. No. 425-32). Swirl to mix.



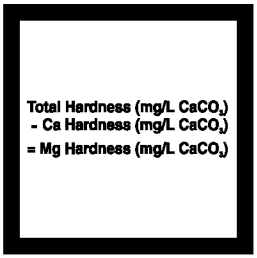
12. Place the delivery tube tip into the solution and swirl the flask while titrating with EDTA from red to pure blue. Record the number of digits required.

Note: *Titrate slowly near the end point because the reaction is slow, especially in colder samples.*

13. Use the appropriate formula below to calculate the final concentration based on sample size and cartridge used:

Digits Required x Digit Multiplier (*Table 1*) = mg/L Total Hardness as $CaCO_3$

Digits Required x Digit Multiplier (*Table 2*) = G.d.h.



14. The first titration gives the mg/L calcium hardness and the second gives the mg/L total hardness. The difference between the values is the mg/L magnesium hardness as $CaCO_3$.

Total Hardness (mg/L $CaCO_3$) - Ca Hardness (mg/L $CaCO_3$) = Mg Hardness (mg/L $CaCO_3$)

Note: *See below for conversion factors.*

Hardness Relationships

$$\text{mg/L Mg Hardness as } CaCO_3 = \text{mg/L Total Hardness as } CaCO_3 - \text{mg/L Ca Hardness as } CaCO_3$$

$$\text{mg/L } MgCO_3 = \text{mg/L Mg Hardness as } CaCO_3 \times 0.842$$

$$\text{mg/L Mg} = \text{mg/L } MgCO_3 \times 0.29$$

Interferences

WARNING:
Do not use potassium cyanide to eliminate interferences because it will generate deadly hydrogen cyanide gas when the sulfuric acid solution is added in step 9.

- Although less common than calcium and magnesium, other polyvalent metal ions cause the same hardness effects and will be included in the results.

- Some transition and heavy metals complex the indicator and prevent the color change at the end point.
- Iron does not interfere up to 15 mg/L. Above this level it causes a red-orange to green end point which is sharp and usable up to 30 mg/L iron. Substitute a 0.0800 M CDTA or 0.800 M CDTA titration cartridge for the 0.0800 M EDTA or 0.800 M EDTA titration cartridges, respectively, if iron interference is probable. For results in G.d.h., divide the mg/L result by 17.9.
- Manganese titrates directly up to 20 mg/L but masks the end point above this level. Adding a 0.1-gram scoop of hydroxylamine hydrochloride raises this level to 200 mg/L manganese.
- Copper interferes at levels of 0.10 and 0.20 mg/L. Cobalt and nickel interfere at all levels and must be absent or masked.
- Orthophosphate causes a slow end point and polyphosphate must be absent for accurate results.
- Acidity and alkalinity at 10,000 mg/L (as $CaCO_3$) do not interfere.
- Saturated sodium chloride solutions do not give a distinct end point, but the titration can be run directly on sea water.
- Adding the contents of one CDTA Magnesium Salt Powder Pillow removes metal interferences at or below the levels shown in *Table 3*.
- If more than one metal is present at or above the concentrations shown in *Table 3*, an additional CDTA Magnesium Salt Powder Pillow may be required.
- Results obtained by this procedure include the hardness contributed by polyvalent metal ions. If the concentration of each metal is known, a correction can be applied to obtain the calcium and magnesium hardness concentration. The hardness (in mg/L as $CaCO_3$) contributed by each mg/L of metal is listed in *Table 4*. Hardness contributed by metals can be subtracted from the total hardness value obtained in

step 13 to determine the calcium and magnesium hardness concentration.

- Barium, strontium and zinc titrate directly.

Table 3

Metal	CDTA Removes Interference Below this Level
Aluminum	50 mg/L
Cobalt	200 mg/L
Copper	100 mg/L
Iron	100 mg/L
Manganese	200 mg/L
Nickel	400 mg/L
Zinc	300 mg/L

Table 4

Metal	Hardness as $CaCO_3$ Contributed by Each mg/L of Metal
Aluminum	3.710
Barium	0.729
Cobalt	1.698
Copper	1.575
Iron	1.792
Manganese	1.822
Nickel	1.705
Strontium	1.142
Zinc	1.531

REQUIRED REAGENTS*

Calcium and Magnesium Hardness Reagent Sets (about 100 tests each)

10-100+ G.d.h. includes: (1) 282-32, (1) 424-32, (1) 928-99, (1) 947-99, (1) 2449-32, (1) 14959-01 24485-00

10-160 mg/L includes: (1) 282-32, (1) 424-32, (1) 928-99, (1) 947-99, (1) 2449-32, (1) 14364-01 24486-00

100-4,000 mg/L includes: 282-32, (1) 424-32, (1) 928-99, (1) 947-99, (1) 2449-32, (1) 14399-01 24487-00

Description	Unit	Cat. No.
CalVer® 2 Indicator Powder Pillows	100/pkg	947-99
Hardness 1 Buffer Solution	100 mL MDB	424-32
ManVer® 2 Hardness Indicator Powder Pillows	100/pkg	928-99
Potassium Hydroxide Standard Solution, 8.00 N	100 mL MDB**	282-32
Sulfuric Acid, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 L	272-56
Select one or more based on sample concentration:		
EDTA Titration Cartridge, 0.0800 M	each	14364-01
EDTA Titration Cartridge, 0.1428 M	each	14960-01
EDTA Titration Cartridge, 0.714 M	each	14959-01
EDTA Titration Cartridge, 0.800 M	each	14399-01

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250 mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, 100 mL	each	508-42

OPTIONAL REAGENTS

CDTA Magnesium Salt Powder Pillows	100/pkg	14080-99
CDTA Titration Cartridge, 0.08 M	each	14402-01
CDTA Titration Cartridge, 0.8 M	each	14403-01
Hardness 2 Test Solution	100 mL MDB	425-32
Hardness Standard Solution, Voluette® Ampules, 10,000 mg/L as $CaCO_3$, 10 mL	16/pkg	2187-10
Hydroxylamine Hydrochloride	113 g	246-14
Nitric Acid, 70%	500 mL	152-49

* Other reagents and apparatus are listed with the specific procedure.

** Marked Dropper Bottle (MDB). Contact Hach for larger sizes.

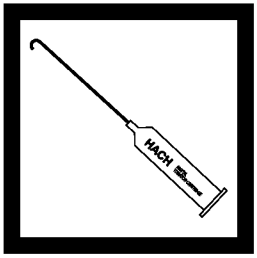
OPTIONAL APPARATUS

Description	Unit	Cat. No.
Bottle, wash, poly, 500 mL	each	620-11
Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
pH Paper, 1.0 to 11 pH	5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10 mL	each	14515-38
Pipet, volumetric, Class A, 20 mL	each	14515-20
Pipet, volumetric, Class A, 25 mL	each	14515-40
Pipet, volumetric, Class A, 50 mL	each	14515-41
Pipet, volumetric, Class A, 100 mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
*sens**ion***™*1* Basic Portable pH Meter with electrode	each	51700-10
Spoon, measuring, 0.1 gram	each	511-00
Spoon, measuring, 0.5 gram	each	907-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

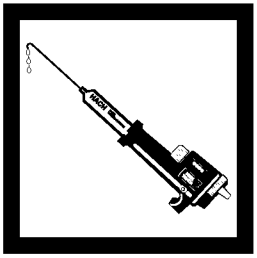
HYPOCHLORITE (Bleach) (50 to 150 g/L [5 to 15%] as Cl2)

Iodometric Method*

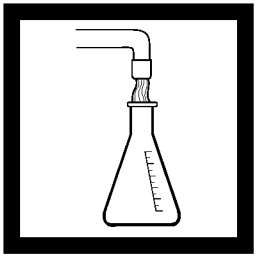
Scope and Application: For testing concentrated liquid bleach (sodium hypochlorite, soda bleach) used as a disinfectant in drinking water or wastewater treatment.



1. Insert a clean delivery tube into the 2.26 N Thiosulfate Titrant Solution cartridge. Attach the cartridge to the titrator body.



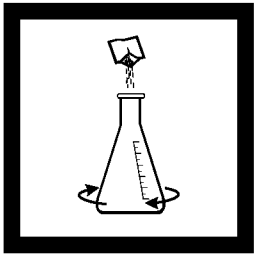
2. Flush the delivery tube by turning the deliver knob to eject a few drops of titrant. Reset the counter to zero and wipe off the tip.



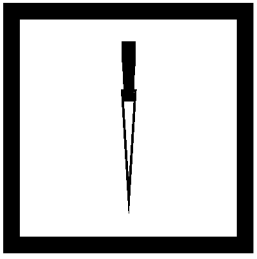
3. Fill a 125-mL Erlenmeyer flask to about the 75-mL mark with deionized or tap water.

Note: *The level of residual chlorine found in tap water will not interfere in the test.*

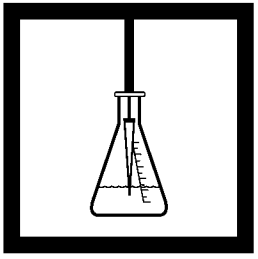
4. Add the contents of one Potassium Iodide Powder Pillow to the flask and swirl to mix.



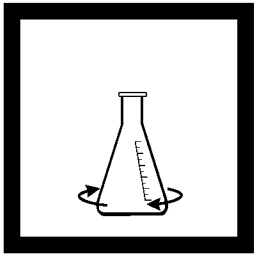
5. Add the contents of one Acid Reagent Powder Pillow to the flask and swirl to mix.



6. Attach a clean tip to the TenSette® Pipet.



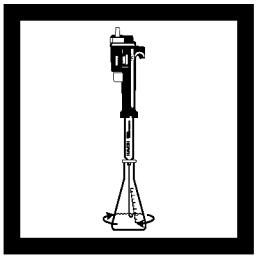
7. Use the pipet to dispense 0.2 mL of bleach sample below the solution level in the flask.



8. Swirl to mix. The solution will turn dark brown.

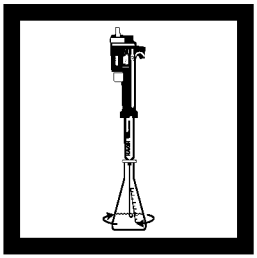
Note: *Proceed immediately with Step 9.*

* Adapted from ASTM method D2022.

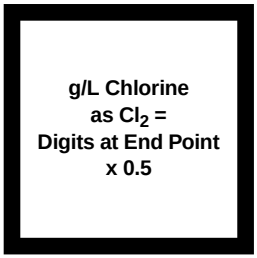


9. Place the delivery tube tip into the solution and swirl the flask while titrating with the thiosulfate titrant until the solution is pale yellow.

10. Add one dropper of Starch Indicator Solution to the flask and swirl to mix. A dark blue or green color will develop.



11. Continue the titration until the solution becomes colorless. Record the number of digits required.



12. Calculate the g/L chlorine:

g/L chlorine = Digits Required x 0.5

Note: *Divide the g/L chlorine by 10 to obtain the % (by volume) chlorine ("trade percent").*

Sample Collection, Preservation and Storage

Soda bleach solutions are relatively unstable. Avoid exposing the sample to heat or light. Collect samples in glass bottles and store in a cool, dark place until analyzed. Analyze as soon as practical.

Accuracy Check

Standard Solution Method

Hach strongly recommends that, for optimum test results, reagent accuracy be checked with each new lot of reagents. The strength of the Thiosulfate Standard Solution can be checked using Potassium Iodide-Iodate Standard Solution:

1. Use a Class A pipet to transfer 50.00 mL of 0.0125 N Potassium Iodide-Iodate Standard Solution to a clean 125-mL Erlenmeyer flask.
2. Add the contents of one Potassium Iodide Powder Pillow to the flask and swirl to mix.
3. Add the contents of three Acid Reagent Powder Pillows to the flask and swirl to mix. Swirl until all powder is dissolved.

4. Continue the titration starting at *step 9* of the procedure. It should take 217–227 digits of 2.26 N Thiosulfate Standard Solution to reach the end point.

Interferences

The iodometric method is relatively free of interferences. The test will determine chlorite ion (ClO_2^-) in addition to the hypochlorite ion (ClO^-). However, the amount of chlorite in commercial bleach is insignificant (typically less than 0.2%).

A large excess of caustic in the bleach sample may lead to low results. After adding the Acid Reagent Powder Pillow (*step 5*), check the pH of the solution with pH paper. The pH should be less than 3. If not, add additional Acid Reagent, one pillow at a time, until the pH drops below 3.

For most accurate results, the temperature of the dilution water (*step 3*) should be less than 20 °C (68 °F).

Precision

In a single laboratory, using a commercial bleach sample of 91.2 g/L (9.12%) Cl_2, a single operator obtained a standard deviation of ± 1.5 g/L (± 0.15%) Cl_2.

Summary of Method

Under acidic conditions, hypochlorite reacts with iodide to produce an equivalent amount of triiodide (I_3^-). The released I_3^- is titrated with standard thiosulfate solution to a colorless end point. The number of digits of thiosulfate required is proportional to the hypochlorite concentration in the original bleach sample.

REQUIRED REAGENTS

HR Hypochlorite (Bleach) Reagent Set (about 100 tests) 26870-00
Includes: (1) 349-32, (1) 1042-99, (1) 20599-96, (1) 26869-01

Description	Unit	Cat. No.
Acid Reagent Powder Pillows	100/pkg	1042-99
Potassium Iodide Powder Pillows	50/pkg	20599-96
Sodium Thiosulfate Standard Titrant Solution, 2.26 N	each	26869-01
Starch Indicator Solution	100 mL MDB*	349-32

REQUIRED APPARATUS

Clippers, large	each	968-00
Delivery Tubes, 180°	5/pkg	17205-00
Digital Titrator Assembly	each	16900-02
Flask, Erlenmeyer, 125-mL	each	505-43
Pipet, TenSette®, 0.1–1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96

OPTIONAL REAGENTS

Potassium Iodide-Iodate Standard Solution, 0.0125 N	1 L	14001-53

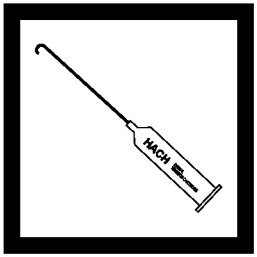
OPTIONAL APPARATUS

pH Paper, 1–11	5/pkg	391-33
Pipet, volumetric, Class A, 50.00 mL	each	14515-41

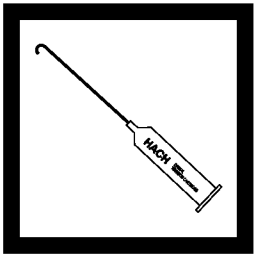
* Marked Dropping Bottle

IRON (10 to 1000 mg/L as Fe)

Using the TitraVer® Titration Cartridge



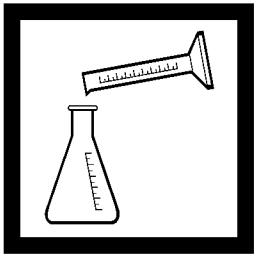
1. Select a sample volume and a TitraVer Titration Cartridge corresponding to the expected iron (Fe) concentration from *Table 1*.



2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step*, for assembly instructions, if necessary.

3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder to measure the sample volume from *Table 1*. Transfer the sample into a clean 125-mL Erlenmeyer flask. Dilute to about the 50-mL mark with deionized water, if necessary.

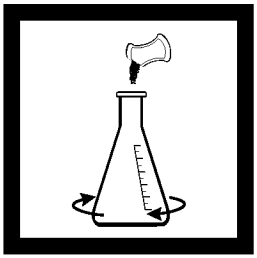
Table 1

Range (mg/L as Fe)	Sample Volume (mL)	Titration Cartridge (M TitraVer)	Catalog Number	Digit Multiplier
10-40	50	0.0716	20817-01	0.1
25-100	20	0.0716	20817-01	0.25
100-400	50	0.716	20818-01	1.0
250-1000	20	0.716	20818-01	2.5

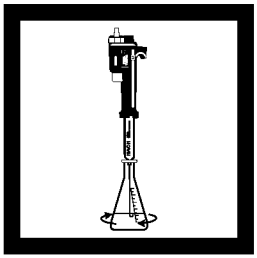
5. Add the contents of one Citrate Buffer Powder Pillow and swirl to mix.

6. Add the contents of one Sodium Periodate Powder Pillow and swirl to mix.

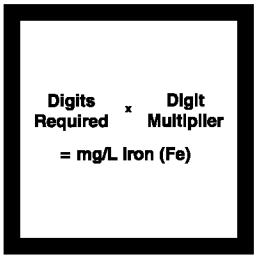
Note: *A yellow color indicates the presence of iron.*



7. Add the contents of one Sulfosalicylic Acid Powder Pillow and swirl to mix. A red color will develop if iron is present.



8. Place the delivery tube tip into the solution and swirl the flask while titrating the sample until the color changes from red to the original yellow. Record the number of digits required.



9. Calculate:

Digits Required x Digit Multiplier = mg/L Iron (Fe)

Accuracy Check

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Use a TenSette® Pipet to add 0.5 mL of 1000 mg/L as Fe standard to the sample in *step 7*. Resume titration back to the same end point. Record the number of additional digits required.

2. Repeat, using two more additions of 0.5 mL. Titrate to the end point after each addition.

3. Each 0.5-mL addition of standard should require 10 additional digits of 0.716 M titrant or 100 digits of 0.0716 M titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Summary of Method

Iron (Fe^{2+}) is oxidized by sodium periodate to the ferric ion (Fe^{3+}). When sulfosalicylic acid is present, the ferric ion forms a red complex, coloring the solution. The red complex is destroyed by titration with EDTA. Citric acid is used to buffer the solution and to stabilize the ferric ion in solution.

REQUIRED REAGENTS

(varies with sample characteristics)
Iron Reagent Sets (about 100 tests)
10-100 mg/L includes: (1) 984-99, (1) 20815-99, (1) 20816-69, (1) 20817-01 24492-00
100-1000 mg/L includes: (1) 984-99, (1) 20815-99, (1) 20816-69, (1) 20818-01 24493-00

Description	Unit	Cat. No.
Citrate Buffer Powder Pillows	100/pkg	20815-99
Sodium Periodate Powder Pillows	100/pkg	984-99
Sulfosalicylic Acid Powder Pillows	100/pkg	20816-69
TitraVer® Standard Solution Titration Cartridge, 0.0716 M	each	20817-01
TitraVer® Standard Solution Titration Cartridge, 0.716 M	each	20818-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Select one or more based on sample concentration:		
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41

OPTIONAL REAGENTS

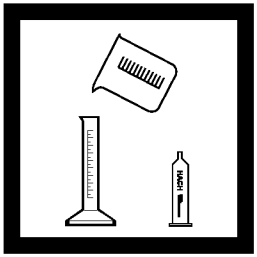
Iron Standard Solution, 1000 mg/L as Fe	100 mL	2271-42

OPTIONAL APPARATUS

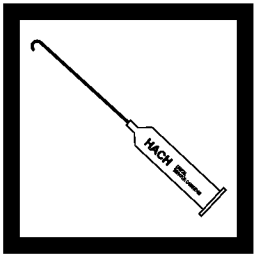
Bottle, wash, poly, 500 mL	each	620-11
Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 25.0 mL	each	14515-40
Pipet, volumetric, Class A, 50.0 mL	each	14515-41
Pipet Filler, safety bulb	each	14651-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

NITRITE (100 to 2500 mg/L as $NaNO_2$)

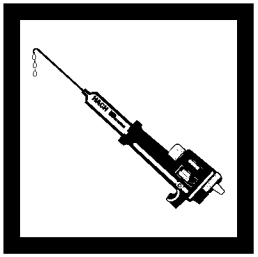
Using Ceric Standard Solution



1. Select the sample volume from *Table 1* which corresponds to the expected sample sodium nitrite concentration (as $NaNO_2$).

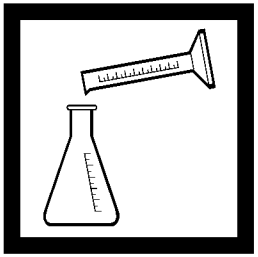


2. Insert a clean delivery tube into the Ceric Standard Solution Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



3. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

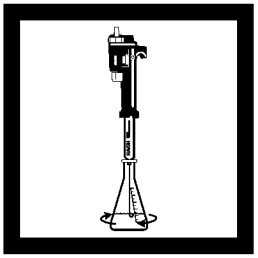


4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample to a clean 125-mL Erlenmeyer flask. Add deionized water to about the 75-mL mark, if necessary.

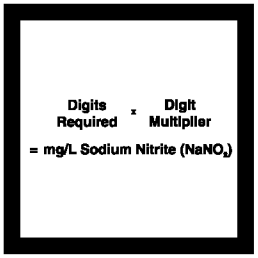
Note: *A pipet is recommended for sample volumes less than 10 mL.*

5. Add five drops of 5.25 N Sulfuric Acid Standard Solution to the flask. Swirl to mix.

6. Add one drop of Ferroin Indicator Solution to the flask. Swirl to mix.



7. Place the delivery tip into the solution. While titrating with Ceric Standard Solution, swirl the flask until the solution color changes from orange to pale blue. Record the number of digits required.



8. Calculate:

Digits Required x Digit Multiplier = mg/L Sodium Nitrite ($NaNO_2$)

Note: *See Standardization of Ceric Solution to verify the normality.*

Table 1

Expected Sample Concentration (as $NaNO_2$)	Sample Volume (mL)	Digit Multiplier
100-400	25	0.86
400-800	10	2.15
800-1500	5	4.31
1500-2500	2	10.78

Standardization of Ceric Solution

The normality of the Ceric Solution will sometimes decrease over time. Before use, verify the normality with the following procedure. This standardization should be done monthly.

1. Use a graduated cylinder or pipet to measure 50 mL of deionized water into a 125-mL Erlenmeyer flask.
2. Add 5 mL of 19.2 N Sulfuric Acid Standard Solution. Swirl to mix.
3. Insert a clean delivery tube into a Ceric Standard Titration Cartridge.
4. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.
5. Place the delivery tube tip into the solution. While swirling the flask, add 200 digits of Ceric Standard.
6. Insert a clean delivery tube into a 0.200 N Sodium Thiosulfate Titration Cartridge.
7. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob until a few drops of titrant are expelled. Reset the counter to zero and wipe the tip.
8. Place the delivery tube tip into the solution. While swirling the flask, titrate with the sodium thiosulfate from an intense yellow color to a faint yellow color. Record the number of

digits required. This step should require about 400-450 digits of titrant.

9. Add one drop of Ferroin Indicator Solution. Swirl to mix. The solution will turn a faint blue.

10. Continue titrating the Ceric Standard Solution (using the 0.20 Sodium Thiosulfate Titration Cartridge) from a faint blue to orange color. Record the number of digits required.

11. Calculate the correction factor:

$$\text{Correction Factor} = \frac{\text{Digits Required}}{500}$$

12. Multiply the mg/L sodium nitrite from *step 8* of the nitrite titration procedure by the correction factor to obtain the correct sodium nitrite concentration.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Prompt analysis is recommended.

If prompt analysis is impossible, store samples for 24 to 48 hours at 4 °C (39 °F) or lower. Warm to room temperature before analysis. Do not use acid preservatives.

Accuracy Check

Dissolve 1.000 gram of fresh sodium nitrite in 100 mL of deionized water. Dilute to 1000 mL with deionized water to prepare a 1000 mg/L sodium nitrite standard solution. Use a 5.0 sample of the standard solution and start with *step 4* of the titration procedure. The analysis should yield 1000 mg/L for *step 8* of the titration procedure.

Summary of Method

Sodium nitrite is titrated with tetravalent cerium ion, a strong oxidant, in the presence of ferroin indicator. After the cerium oxidizes the nitrite, it oxidizes the indicator, causing a color change from orange to pale blue. The concentration of sodium nitrite is proportional to the amount of titrant used.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Ceric Standard Solution Titration Cartridge, 0.5 N	each	22707-01
Ferroin Indicator Solution	29 mL DB	1812-33
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Select one or more based on sample volume:		
Cylinder, graduated, 100 mL, poly	each	1081-42
Pipet, serological, 10 mL	25/pkg	20931-28

REQUIRED APPARATUS (Using Titrastir® Stir Plate Modification)

Delivery Tubes, 90° with hook	5/pkg	41578-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Stir Bar, octagonal, Teflon-coated, 50.8 x 7.9 mm	each	20953-55
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

OPTIONAL REAGENTS

Sodium Thiosulfate Titration Cartridge, 0.200 N	each	22675-01
Sodium Nitrite, ACS	454 g	2452-01
Sulfuric Acid Standard Solution, 19.2 N	100 mL	2038-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Balance, electronic, analytical	each	22310-00
Flask, volumetric, Class A, 50 mL	each	14547-41

OXYGEN, DISSOLVED (1 to greater than 10 mg/L as DO)

Azide Modification of Winkler Method

Using a 300-mL BOD Bottle — Method 8215

1. Collect a water sample in a clean 300-mL BOD Bottle.

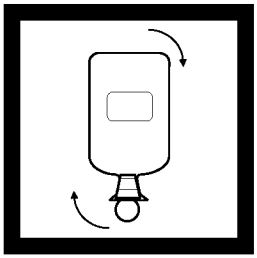
Note: *Allow the sample to overflow the bottle for 2-3 minutes to ensure air bubbles are not trapped.*

Note: *If samples cannot be analyzed immediately, see Sampling and Storage on page 152.*

2. Add the contents of one Manganous Sulfate Powder Pillow and one Alkaline Iodide-Azide Reagent Powder Pillow.

3. Immediately insert the stopper so air is not trapped in the bottle. Invert several times to mix.

Note: *A flocculent precipitate will form. It will be orange-brown if oxygen is present or white if oxygen is absent. The floc settles slowly in salt water and normally requires 5 additional minutes before proceeding to step 5.*

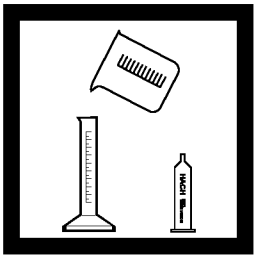


4. Wait until the floc in the solution has settled. Again invert the bottle several times and wait until the floc has settled.

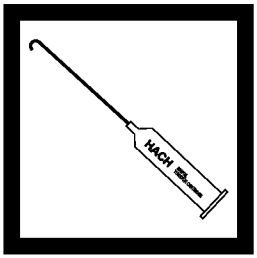
Note: *Waiting until floc has settled twice assures complete reaction of the sample and reagents.*

5. Remove the stopper and add the contents of one Sulfamic Acid Powder Pillow. Replace the stopper without trapping air in the bottle and invert several times.

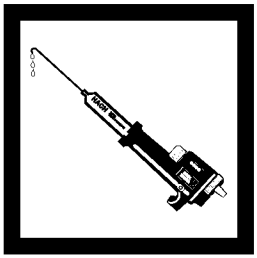
Note: *The floc will dissolve and leave a yellow color if oxygen is present.*



6. Select a sample volume and Sodium Thiosulfate Titration Cartridge corresponding to the expected dissolved oxygen (D.O.) concentration from *Table 1*.

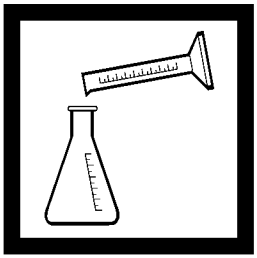


7. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.

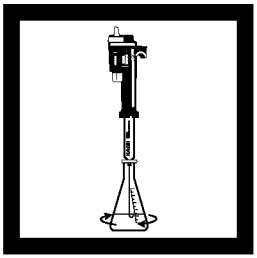


8. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

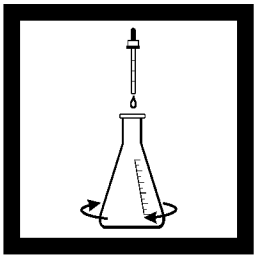
Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



9. Use a graduated cylinder to measure the sample volume from *Table 1*. Transfer the sample into a 250-mL Erlenmeyer flask.

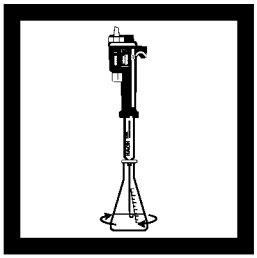


10. Place the delivery tube tip into the solution and swirl the flask while titrating with sodium thiosulfate to a pale yellow color.

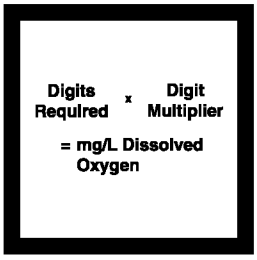


11. Add two 1-mL droppers of Starch Indicator Solution and swirl to mix.

Note: *A dark blue color will develop.*



12. Continue the titration to a colorless end point. Record the number of digits required.



13. Calculate:

Digits Required x Digit Multiplier = mg/L Dissolved Oxygen

Table 1

Range (mg/L D.O.)	Sample Volume (mL)	Titration Cartridge (N $Na_2S_2O_3$)	Catalog Number	Digit Multiplier
1-5	200	0.200	22675-01	0.01
2-10	100	0.200	22675-01	0.02
>10	200	2.000	14401-01	0.1

Using a 60-mL BOD Bottle **Method 8332**

1. Collect a water sample in a clean 60-mL glass-stoppered BOD Bottle.

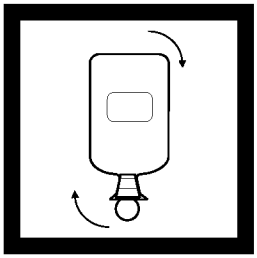
Note: *Allow the sample to overflow the bottle for 2-3 minutes to ensure air bubbles are not trapped.*

Note: *If samples cannot be analyzed immediately, see Sampling and Storage on page 152.*

2. Add the contents of one Dissolved Oxygen 1 Reagent Powder Pillow and one Dissolved Oxygen 2 Reagent Powder Pillow.

3. Immediately insert the stopper so air is not trapped in the bottle. Invert several times to mix.

Note: *A flocculent precipitate will form. It will be orange-brown if oxygen is present or white if oxygen is absent. The floc settles slowly in salt water and normally requires 5 additional minutes before proceeding to step 5.*

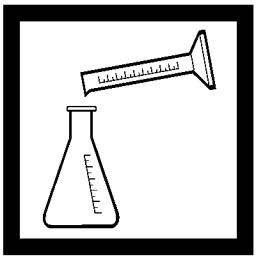


4. Wait until the floc in the solution has settled and the top half of the solution is clear. Again invert the bottle several times and wait until the floc has settled.

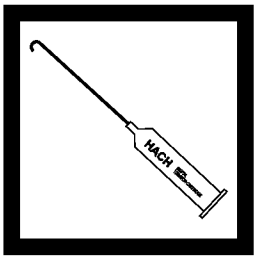
Note: *Results are not affected if the floc does not settle or if some of the reagent powder does not dissolve.*

5. Remove the stopper and add the contents of one Dissolved Oxygen 3 Powder Pillow. Replace the stopper without trapping air in the bottle and invert several times to mix.

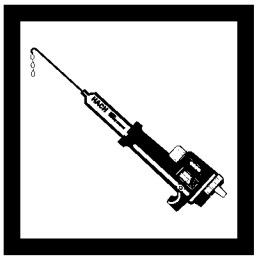
Note: *The floc will dissolve and leave a yellow color if oxygen is present.*



6. Accurately measure 20 mL of the prepared sample and transfer it to a 125-mL Erlenmeyer flask.

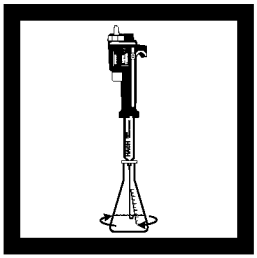


7. Attach a clean straight-stem delivery tube to a 0.2000 N Sodium Thiosulfate Titration Cartridge. Twist the cartridge onto the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary

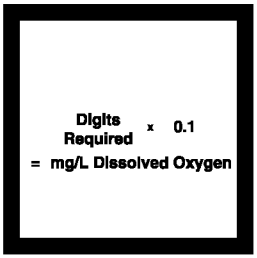


8. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir Stir Plate. See General Description, Step 3 in Step-by-Step.*



9. Titrate the prepared solution with 0.2000 N Sodium Thiosulfate until the sample changes from yellow to colorless. Record the number of digits.



10. Calculate:

Digits required x 0.1 = mg/L Dissolved Oxygen

Sampling and Storage

Sampling and sample handling are important in obtaining meaningful results. The dissolved oxygen content of the sample changes with depth, turbulence, temperature, sludge deposits, light, microbial action, mixing, travel time, and other factors. A single dissolved oxygen test rarely reflects the over-all condition of a body of water. Several samples taken at different times, locations and depths are recommended for most reliable results.

Collect samples in clean BOD Bottles (see *step 1*). If storage is necessary, run steps 1-5 of the procedure and store in the dark at 10-20 ° C. Seal the bottle with water by pouring a small volume of water into the flared lip area of a stopper bottle. Snap a BOD Bottle Cap over the flared lip. Samples preserved like this can be held 4-8 hours. Begin with *step 6* when analyzing.

Accuracy Check

Check the strength of the Sodium Thiosulfate Solution by using an Iodate-Iodide Standard Solution which is equivalent to 10 mg/L dissolved oxygen. For the 300-mL procedure, begin at *step 5* adding the Sulfamic Acid Powder Pillow. For the 60-mg/L procedure, begin the analysis at *step 5* adding the Dissolved Oxygen 3 Powder Pillow. The titration should take 10 mL. If

more than 10.5 mL is required to reach the end point, replace the Sodium Thiosulfate Solution.

Interferences

Nitrite interference is eliminated by the azide in the reagents. Other reducing or oxidizing substances may interfere. If these are present, use an alternate method, such as the High Range Dissolved Oxygen Method (colorimetric) in this manual, or a dissolved oxygen electrode.

Summary of Method

Samples are treated with manganous sulfate and alkaline iodide-azide reagent to form an orange-brown precipitate. Upon acidification of the sample, this floc reacts with iodide to produce free iodine as triiodide in proportion to the oxygen concentration. The iodine is titrated with sodium thiosulfate to a colorless end point.

REQUIRED REAGENTS FOR 300-ML BOD BOTTLE

(Varies with sample characteristics)

Dissolved Oxygen Reagent Set (about 50 tests) 22722-00
Includes: (1) 349-32, (2) 1071-68, (2) 1072-68, (1) 22675-01, (2) 20762-68

Description	Unit	Cat. No.
Alkaline Iodide-Azide Powder Pillows	25/pkg	1072-68
Manganous Sulfate Powder Pillows	25/pkg	1071-68
Sodium Thiosulfate Titration Cartridge, 0.2000 N	each	22675-01
Sodium Thiosulfate Titration Cartridge. 2.00 N	each	14401-01
Starch Indicator Solution	100 mL MDB*	349-32
Sulfamic Acid Powder Pillows	25/pkg	20762-68

REQUIRED APPARATUS FOR 300-ML BOD BOTTLE

Bottle, with stopper, BOD, 300-mL	each	621-00
Clippers, for opening pillows	each	968-00
Cylinder, graduated, 250-mL	each	508-46
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46

* Contact Hach for larger sizes.

REQUIRED REAGENTS FOR 60-ML BOD BOTTLE

Description	Unit	Cat. No.
Dissolved Oxygen 1 Reagent Powder Pillows	100/pkg	981-99
Dissolved Oxygen 2 Reagent Powder Pillows	100/pkg	982-99
Dissolved Oxygen 3 Reagent Powder Pillows	25/pkg	987-68
Sodium Thiosulfate Titration Cartridge, 0.2000 N	each	22675-01

REQUIRED APPARATUS FOR 60-ML BOD BOTTLE

Bottle, with stopper, BOD, 60-mL	each	1909-02
Clippers, for opening pillows	each	968-00
Cylinder, graduated, 50-mL	each	1081-41
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43

OPTIONAL REAGENTS

Iodate-Iodide Standard Solution, 10 mg/L as DO	500 mL*	401-49

OPTIONAL APPARATUS

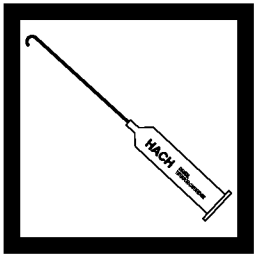
Cap, BOD Bottle, plastic	6/pkg	2419-06
Clamp Holder	each	326-00
Clamp, 2-prong, extension, 38 mm	each	21145-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
Sewage Sampler, Lab-Line	each	427-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

Procedures and kits for portable dissolved oxygen measurements using this method are available from Hach.

* Contact Hach for larger sizes.

SALINITY (0 to 100 ppt* as Salinity)

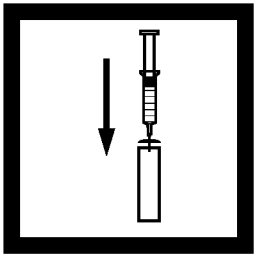
Using Mercuric Nitrate



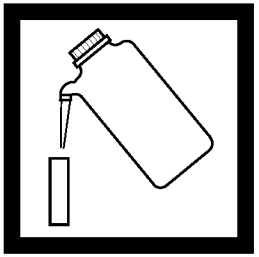
1. Insert a clean, straight-stem delivery tube to a Mercuric Nitrate Titration Cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.

2. Flush out the delivery tube by turning the knob until titrant begins flowing from the end of the tube. Wipe the tip and reset the counter to zero.

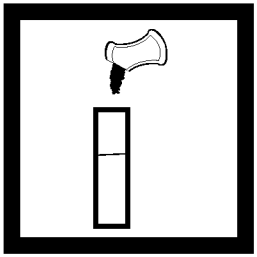
Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



3. Using the 3-mL (3-cc) syringe, collect a 2.0-mL water sample. Add to the vial provided.

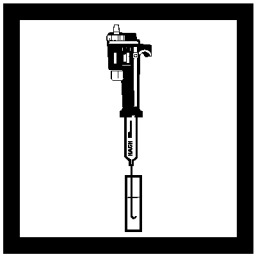


4. Fill the vial to the 10-mL mark with deionized water.



5. Add the contents of one Diphenylcarbazone Reagent Powder Pillow to the vial and mix.

Note: *Results will not be affected if a small portion of the diphenylcarbazone reagent powder does not dissolve.*



6. Titrate the sample with mercuric nitrate until the color changes from yellow to light pink.

Record the number of digits.

7. Determine the salinity of the water sample in parts per thousand (ppt) by multiplying the reading by 0.1.

Note: *Results may be expressed as mg/L Cl^- by multiplying the ppt salinity by 569. Results may be expressed as mg/L NaCl by multiplying the ppt salinity by 940.*

* ppt = parts per thousand

Summary of Method

The mercuric nitrate method of chloride analysis has become popular due to the sharp yellow to pinkish-purple end point of diphenylcarbazone. A single, stable powder has been developed, combining the color indicator with an appropriate buffer to establish the correct pH.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Diphenylcarbazone Reagent Powder Pillows	100/pkg	967-99
Mercuric Nitrate Titration Cartridge, 2.570 N	each	23937-01

REQUIRED APPARATUS

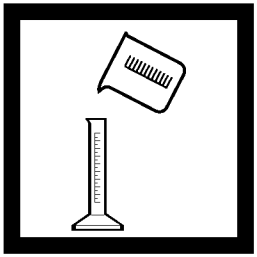
Vial, 2, 5, 10, 15, 20, 25-mL marks	each	2193-00
Syringe, 3 cc, Luer lock tip	each	43213-00
Demineralizer Assembly, 473 mL	each	21846-00

OPTIONAL APPARATUS

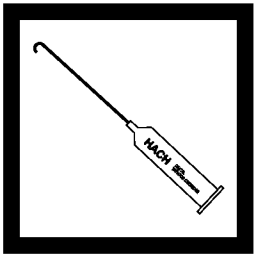
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

SULFITE (4 to greater than 400 mg/L as SO_3^{2-})

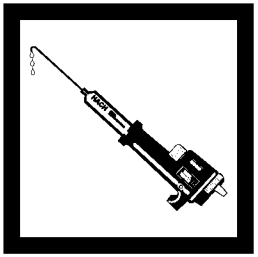
Using Iodate-Iodide



1. Select a sample volume corresponding to the expected sulfite (SO_3^{2-}) concentration from *Table 1*.

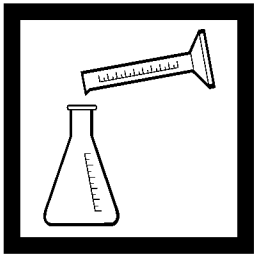


2. Insert a clean delivery tube into the Iodate-Iodide Titration Cartridge (KIO_3-KI). Attach the cartridge to the titrator body. See *General Description, Step-by-Step*, for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 125-mL Erlenmeyer flask. Dilute to about the 50-mL mark with deionized water.

Note: *Avoid unnecessary agitation throughout the procedure.*

Note: *See Sampling and Storage on page 158.*

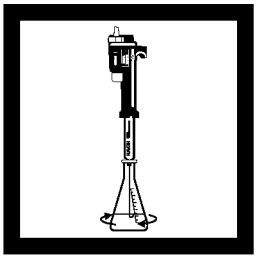
Table 1

Range (mg/L as SO_3^{2-})	Sample Volume (mL)	Titration Cartridge (N KIO_3-KI)	Catalog Number	Digit Multiplier
Up to 160	50	0.3998	14961-01	0.4
100-400	20	0.3998	14961-01	1.0
200-800	10	0.3998	14961-01	2.0
>400	5	0.3998	14961-01	4.0

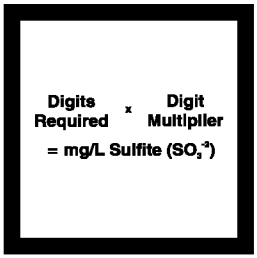
5. Add the contents of one Dissolved Oxygen 3 Reagent Powder Pillow and swirl gently to mix.

Note: *0.5 mL of 19.2 N Sulfuric Acid Standard Solution may be substituted for the powder pillow.*

6. Add one dropperful of Starch Indicator Solution and swirl to mix.



7. Place the delivery tube tip into the solution and swirl the flask while titrating with the iodate-iodide to a permanent blue end point. Record the number of digits required.



8. Calculate:

Digits Required x Digit Multiplier = mg/L Sulfite (SO_3^{2-})

Note: *To obtain the concentration of other sulfite forms, multiply the mg/L SO_3^{2-} determined in step 8 by the appropriate multiplier from Table 2.*

Table 2

Form	Multiplier
Bisulfite, Hydrogen Sulfite (HSO_3^-)	1.01
Sodium Bisulfite, Sodium Hydrogen Sulfite ($NaHSO_3$)	1.30
Sodium Metabisulfite, Sodium Pyrosulfite ($Na_2S_2O_5$)	1.19
Sodium Sulfite (Na_2SO_3)	1.58

Sampling and Storage

Samples must be analyzed immediately. Cool hot samples to 50 °C or lower.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Sulfite Standard Solution Voluette® Ampule, 5,000 mg/L SO_3^{2-}.

2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in *step 7*. Resume titration back to the same end point. Record the number of digits required.

3. Repeat, using additions of 0.2 and 0.3 mL, titrating to the end point after each.

4. Each 0.1 mL addition of standard should require 25 additional digits of titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

A standard solution equivalent to 40 mg/L sulfite can be prepared by diluting 10.0 mL of 0.025 N Sodium Thiosulfate Titrant to 250 mL in a volumetric flask. Titrate a 50 mL sample, using the above procedure.

Interferences

Sulfide, organic matter and other oxidizable substances will cause positive error in the titration. Nitrite will react with sulfite to cause low results. Some metals, especially copper, catalyze the oxidation of sulfite to sulfate. Addition of one Dissolved Oxygen 3 Powder Pillow per liter of sample immediately upon sampling will help eliminate the effects of nitrite and copper.

Summary of Method

Sulfite ion is titrated with potassium iodate-iodide standard solution under acidic conditions to a blue starch end point. The volume of titrant used is proportional to the sulfite concentration.

REQUIRED REAGENTS

Sulfite Reagent Set (about 100 tests) 22723-00
Includes: (1) 349-32, (1) 987-99, (1) 14961-01

Description	Unit	Cat. No.
Dissolved Oxygen 3 Reagent Powder Pillows	100/pkg	987-99
Iodate-Iodide Titration Cartridge, 0.3998 N	each	14961-01
Starch Indicator Solution	100 mL MDB*	349-32
Water, deionized	4 L	272-56

* Contact Hach for larger sizes.

REQUIRED APPARATUS

Description	Unit	Cat. No.
Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 125 mL	each	505-43
Select one or more based on sample concentration:		
Cylinder, graduated, 10 mL	each	508-38
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 50 mL	each	508-41

OPTIONAL REAGENTS

Sodium Thiosulfate Standard Solution, 0.025 N	1000 mL	24093-53
Sulfite Standard Solution, Voluette® Ampules, 5,000 mg/L SO_3 10 mL	16/pkg	14267-10
Sulfuric Acid Standard Solution, 19.2 N	100 mL MDB	2038-32

OPTIONAL APPARATUS

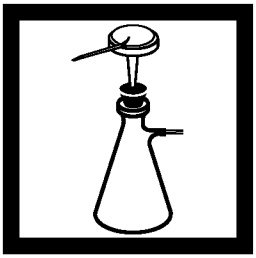
Bottle, wash poly, 500 mL	each	620-11
Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
Flask, volumetric, Class B, 250 mL	each	547-46
Pipet, TenSette® 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 5 mL	each	14515-37
Pipet, volumetric, Class A, 10 mL	each	14515-38
Pipet, volumetric, Class A, 20 mL	each	14515-20
Pipet, volumetric, Class A, 50 mL	each	14515-41
Pipet Filler, safety bulb	each	14651-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

TURBIDITY STANDARDS

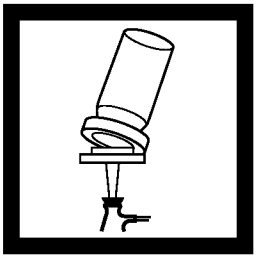
Preparing Turbidity-Free Water

Phase 1: Filtration Assembly

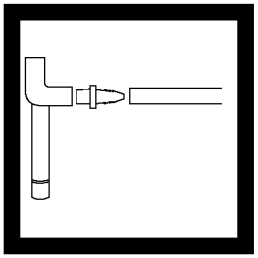
1. Attach the filter funnel stem to a 1000-mL filtering flask.



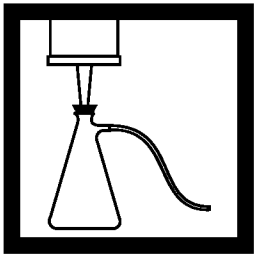
2. Using plastic tweezers, position a 0.45 micron membrane filter on top of the funnel stem.



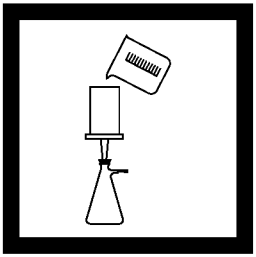
3. Cover the stem with the filter housing.



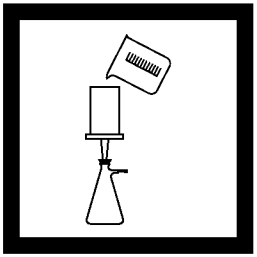
4. Attach a vacuum hose to the water aspirator and turn on water.



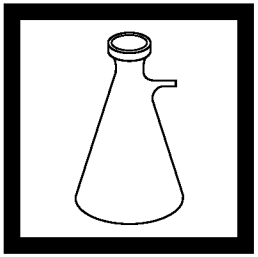
5. Attach the vacuum hose to the sidearm.



6. Pour a total of about 800 mL, in three portions, of deionized water through the filter funnel and wait until it passes through the filter. Discard this rinse water.

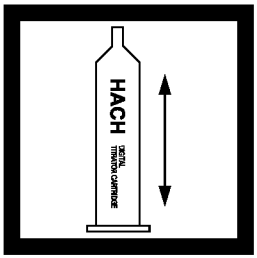


7. Again add 800 mL of deionized water through the filter funnel and collect in a filter flask. Remove vacuum hose from sidearm and turn off water.

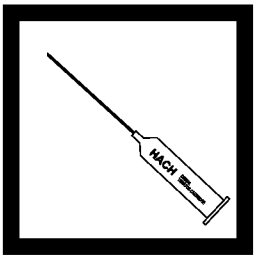


8. Use this filtered deionized water for all formazin dilutions.

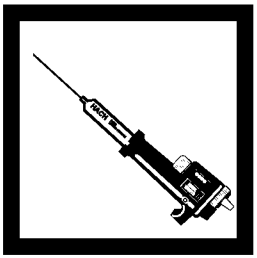
Phase 2: Preparing Standards using a Formazin Cartridge



1. Shake the Formazin Cartridge vigorously for one minute to mix the formazin suspension.

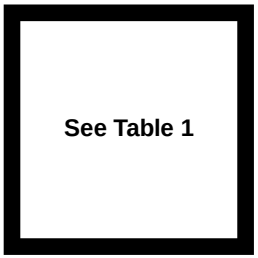


2. Attach a clean delivery tube to the 4000 NTU Formazin Cartridge. Cut the hooked end off the delivery tube with clippers. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.



3. Flush the delivery tube by turning the delivery knob until a few drops of formazin are ejected from the tube. Zero the counter and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Select the standard concentration from the list below. Dispense the formazin into a clean Class A volumetric flask. Dilute with turbidity-free water to the mark and mix well. Refer to the table below for the standard(s) you require.

Table 1

Formazin Standard Concentration (NTU)	Number of Digits Required	Flask Size
100	1000	50-mL
40	400	50-mL
10	100	50-mL
4	80	100-mL

Prepararation of a 1 NTU Formazin Standard

There will be a residual amount of turbidity in even the purest water used to make formazin dilutions. At the 1 NTU level this can affect the value of the formazin standard significantly, causing a positive error. The following procedure corrects for the turbidity of the dilution water when making a 1 NTU formazin standard in a 500-mL, Class A, volumetric flask.

1. Standardize the turbidimeter with a secondary standard on a range appropriate for the measurement of the dilution water, usually the 0-1 NTU range.

2. Measure and record the turbidity of the dilution water to be used in making the 1 NTU formazin standard.

3. Calculate the number of digits necessary to dispense the proper amount of formazin into a 500-mL, Class A, volumetric flask for a 1 NTU formazin standard:

   $$DIGITS = 100(1 - T_W)$$

   Where:

   T_W is the turbidity of the dilution water

4. Carefully dispense the calculated number of digits into a 500-mL volumetric flask. Dilute with dilution water to the 500-mL mark and mix well.

Preparation of any Formazin Standard

The following formula may be used to determine the correct number of digits necessary to dispense formazin for a standard of any value.

$$DIGITS = (0.2)(V)(T_D - T_W)$$

Where:

T_D = desired turbidity of the formazin standard

T_W = turbidity of the dilution water (this term may be dropped if it is 1% or less of the TD value)

V = volume of the flask in mL

Example 1:
One liter of a 0.5 NTU formazin standard is required. It is found that the dilution water has a turbidity of 0.05 NTU. Because the dilution water turbidity is 10% of the desired standard, the dilution water correction must be made.

The number of digits of formazin is equal to:

DIGITS = (0.2) (1000.0) (0.5-0.05) = 90

Thus, 90 digits of formazin dispensed in a 1000 mL, Class A, volumetric flask and diluted to volume with 0.05 NTU water will give a 0.5 NTU formazin standard. The size of the volumetric flask should be chosen so that the number of digits calculated is approximately 100 or more.

Example 2:
50 mL of a 50 NTU formazin standard is required. It is found that the dilution water is 0.1 NTU. Because the dilution water is only 0.2% of the desired standard, the dilution water correction can be ignored.

The number of digits necessary to dispense the formazin is:

DIGITS = (0.2) (50.0) (50) = 500

500 digits of formazin diluted with 50.0 mL of dilution water will give a 50 NTU formazin standard.

Interferences

Because dirty or scratched glassware, air bubbles and color in a sample will interfere with turbidity measurements, sample cells must be scratch-free and samples should be colorless without air bubbles.

Summary of Method

The measurement of turbidity is based on the scattering of light by the suspended particles (clay, sand, bacteria) in solution. The amount of light scattered at 90° to the incident light is directly proportional to the turbidity.

Turbidity is measured in nephelometric turbidity units (NTUs). These units of measurement are based on the amount of light scattered by particles of a polymer reference standard called

formazin. Formazin, a mixture of hydrazine sulfate and hexamethylenetetramine, produces particles which scatter light in a reproducible manner.

The Hach 4000 NTU Formazin Cartridge, when used with the Hach Digital Titrator, offers a quick, yet accurate method for the preparation of formazin standards used in turbidimeter calibration.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Formazin Titration Cartridge, 4000 NTU	each	2461-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

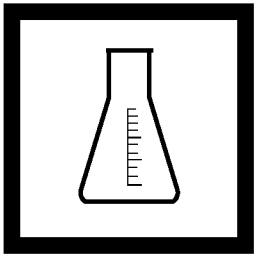
Clippers, for opening pillows	each	968-00
Digital Titrator	each	16900-01
Filter Holder, 47 mm, magnetic base	each	13529-00
Aspirator, vacuum pump, poly	each	2131-00
Filters, membrane, 0.45 microns	100/pkg	13530-00
Flask, filtering, 1000 mL	each	546-53
Flask, volumetric, Class A, 50 mL	each	14574-41
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 500 mL	each	14574-49
Stopper, rubber, No. 7, one hole	6/pkg	2119-07
Tubing, rubber, 2.4 mm ID	12 ft	560-19
Tweezers, plastic	each	14282-00

OPTIONAL APPARATUS

Bottle, wash poly, 500 mL	each	620-11
Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473 mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

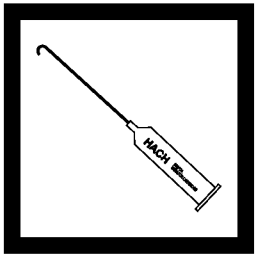
VOLATILE ACIDS

Using Sodium Hydroxide



1. Distill the sample and collect 150 mL of distillate.

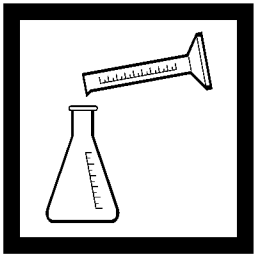
Note: *Use the Volatile Acids Procedure, Sample Distillation, accompanying the General Purpose Distillation Apparatus Set or the distillation procedure described in Standard Methods for the Examination of Water and Wastewater.*



2. Attach a clean delivery tube to a 0.9274 N Sodium Hydroxide titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step,* for assembly instructions, if necessary.

3. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*

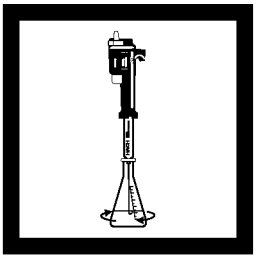


4. Select the distillate volume corresponding to the expected volatile acids concentration as acetic acid from *Table 1*. Using a graduated cylinder, transfer the distillate volume into a clean 250-mL Erlenmeyer flask and dilute to about the 150-mL mark with deionized water.

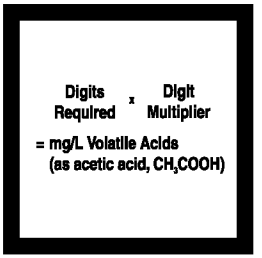
Table 1

Range (mg/L as CH_3COOH)	Volume (mL)	Titration Cartridge (N NaOH)	Catalog Number	Digit Multiplier
100-400	150	0.9274	14842-01	1
200-800	75	0.9274	14842-01	2
600-2400	25	0.9274	14842-01	6

5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.



6. Place the delivery tube tip into the solution and swirl while titrating with sodium hydroxide until a light pink color appears. Record the number of digits required.



7. Calculate:

Digits Required x Digits Multiplier = mg/L Volatile Acids (as acetic acid, CH_3COOH)

Note: *Approximately 70% of the volatile acids in the sample will be found in the distillate. This has been accounted for in the calculation.*

Summary of Method

A sample acidified with sulfuric acid is distilled and the distillate titrated to the phenolphthalein end point with sodium hydroxide standard.

REQUIRED REAGENTS

Volatile Acids Reagent Set (about 100 tests) 24602-00
Includes: (1) 942-99, (1) 14842-01

Description	Unit	Cat. No.
Phenolphthalein Indicator Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 0.9274 N	each	14842-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, 250 mL	each	508-46
Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250 mL	each	505-46

OPTIONAL APPARATUS

Clamp, 2-prong, extension, 38 mm	each	21145-00
Clamp Holder	each	326-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook	5/pkg	41578-00
Distillation Heater and Support Apparatus, 115 Vac	each	22744-00
Distillation Heater and Support Apparatus, 230 Vac	each	22744-02
Distillation Apparatus Set	each	22653-00
Standard Methods for the Examination of Water and Wastewater, 19th ed.	each	22708-00
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10

APPENDIX A
ACCURACY CHECK AND STANDARD ADDITIONS

Most of the procedures in this manual have an accuracy check based on the standard additions method. Standard additions is a widely accepted technique for checking the validity of test results. Also known as “spiking” and “known additions,” the technique adds a small amount of the component (parameter) being measured to an analyzed sample and the analysis is repeated. The increase in the test results should equal the amount of the standard added. The results can be used to check the performance of the reagents, the apparatus, and the procedure.

First Step - The Accuracy Check

Perform the procedure and accuracy check as described in this manual. In each accuracy check the number of digits expected for each increment is given. If the actual number of digits required is within 1% of the expected number of digits, the analyst can conclude the answer for the sample is accurate and the reagents, apparatus, and method used are working properly.

Second Step - The Decision Tree

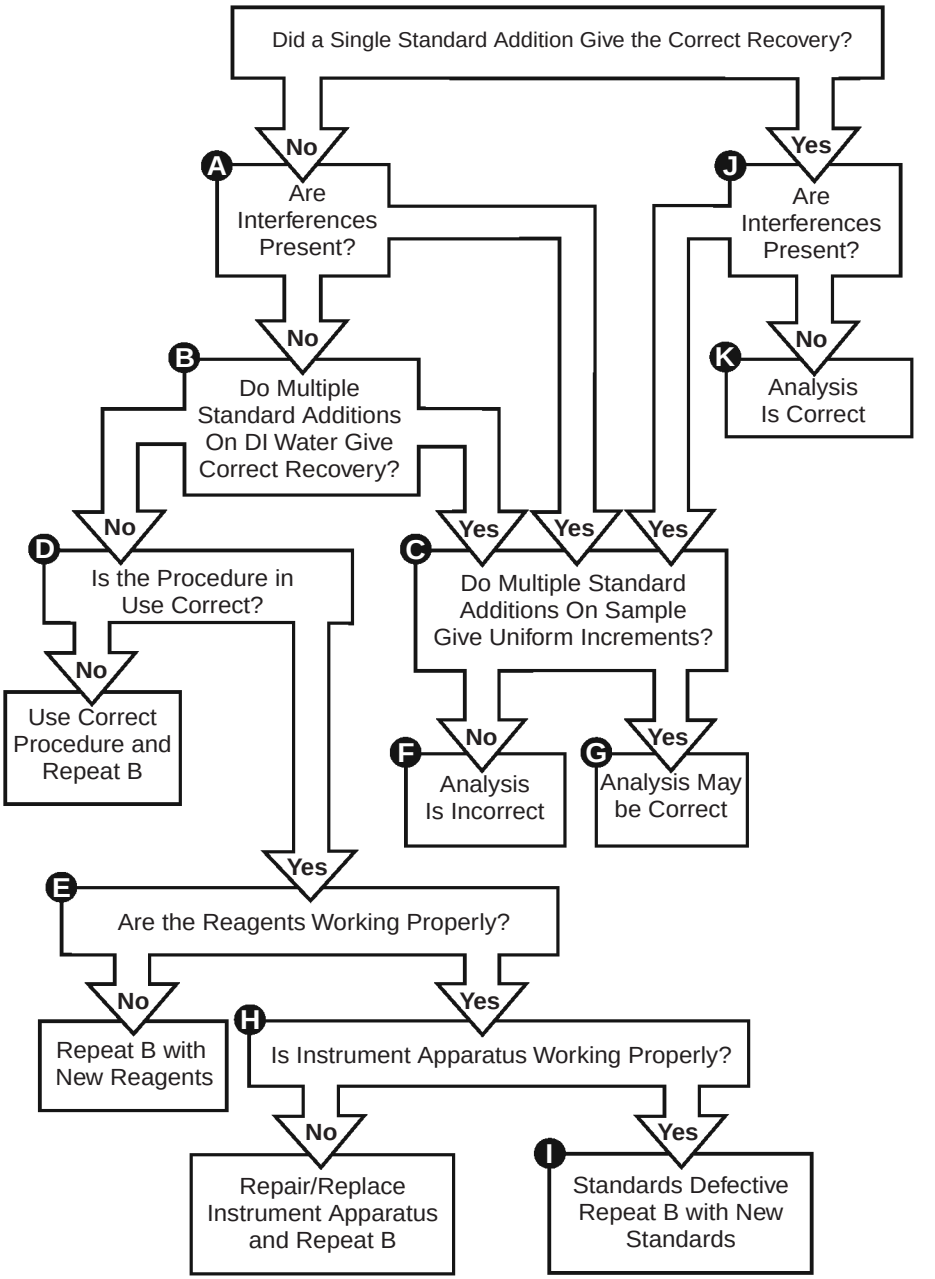
If the actual number of digits varies noticeably, then it must be concluded the problem was caused by either the reagents, the apparatus, the procedure or an interfering substance. By following a logical troubleshooting approach, the source of the problem can be systematically determined. Using the step-by-step decision tree in *Figure 1* will greatly ease identifying the problem. An explanation of each step in the decision tree follows.

Third Step - The Branches

Branch A

Suppose the first, or all three standard additions to the sample did not give the correct incremental digit increase. A possible cause for this could be the presence of interferences. Other causes could be defective reagents, an incorrect procedure, defective apparatus or a defective standard used for standard addition. If interferences are either absent or assumed to be absent, proceed to Branch B. If interferences are present, proceed to Branch C. The Chloride Procedure, Silver Nitrate Method, is used as an example throughout these steps.

Figure 1
Decision Tree



Branch B

Repeat the Accuracy Check given in the procedure substituting the same volume of deionized water for the sample. For example, using the Chloride Procedure, Silver Nitrate Method:

1. Take a 50.0-mL sample of deionized water and follow the Chloride Procedure, Silver Nitrate Method. Record the number of digits required for the titration.

2. Add 0.10 mL of Chloride Standard Solution, 12,500 mg/L, and titrate to the end point. Record the number of digits required for the titration.

3. Repeat, using two more additions of 0.1 mL of 12,500 chloride standard, titrating to the end point after each addition. Record the number of digits required.

4. Tabulate the date as shown below:

Table 1

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	_____	0	_____
0.1	_____	_____	_____
0.2	_____	_____	_____
0.3	_____	_____	_____

The **Total Standard Added (mL)** will vary depending on the procedure used.

The **Total Number of Digits Used** are the total digits recorded after each titration.

The **Total Standard Added (mg/L)** is determined for each addition by the following equation:

$$\frac{\text{Total Standard Added (mL)}}{\text{Sample Volume (mL)}} \times \text{Standard Concentration (mg/L)} = \text{Total Standard Added (mg/L)}$$

The **Total Parameter Found (mg/L)** is determined by following the calculation step of the procedure used. Use the same volume of

deionized water as used for the sample. The addition of standard will not change the digit multiplier.

Performing the above procedure, the completed table would look like this:

Table 2

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	0	0	0
0.1	25	25	25
0.2	50	50	50
0.3	75	75	75

To complete the table the following calculations were made based on the above formula:

First Addition

$$\frac{0.1}{50} \times 12{,}500 = \text{Total Standard Added (mg/L)} = 25 \text{ mg/L}$$

Second Addition

$$0.1 + 0.1 = 0.2 \text{ mL} = \text{Total Standard Added (mL)}$$

0.2 mL in the above formula gives 50 mg/L total standard added.

Third Addition

$$0.1 + 0.1 + 0.1 = 0.3 \text{ mL} = \text{Total Standard Added (mL)}$$

0.3 mL in the above formula gives 75 mg/L total standard added.

The data shown above reveals several points:

- The chemicals, apparatus, procedures and standards are in good working condition. This conclusion is made because chloride added to the deionized water sample was recovered entirely in the same uniform steps of addition.
- Because chloride added to deionized water was recovered, but was not recovered during the Accuracy Check, one may

conclude the sample contains interferences which prevent the test reagents from operating properly.

- The first analysis of the water sample gave an incorrect result.

If the above results gave the expected increments between additions, proceed to Branch C. If the results did not give the expected increments, proceed to Branch D.

Branch C

If interfering ions are present, it may be concluded the analysis is incorrect. However, with the completed accuracy check it may be possible to arrive at an approximation of the correct result. Tabulate the results as follows:

Table 3

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	_____	0	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

The **Total Standard Added (mL)** will vary depending on the procedure used.

The **Total Number of Digits Used** are the total digits recorded after each addition of standard as specified in the accuracy check.

The **Total Standard Added (mg/L)** is determined for each addition by the following equation:

$$\frac{\text{Total Standard Added (mL)}}{\text{Sample Volume (mL)}} \times \text{Standard Concentration (mg/L)} = \text{Total Standard Added (mg/L)}$$

The **Total Parameter Found (mg/L)** is determined by following the calculation step of the procedure used. Use the same volume of deionized water as used for the sample. The addition of standard will not change the digit multiplier.

If steps between each addition are roughly uniform (i.e., 25 digits or 25 mg/L difference between each addition), proceed to Branch

G. If the results are not uniform (i.e., 13, 10, and 6 mg/L), proceed to Branch F.

For example, a sample of water was analyzed for chloride with the result being 100 mg/L. The analyst, suspecting interferences, made one standard addition of 0.10 mL of 12,500-mg/L chloride standard to 50.0 mL of sample. Rather than an increase of 25 mg/L as expected, the analyst found an increase of 13 mg/L.

The analyst added a second and third addition of 0.1 mL of standard. The titrations were made and the results tabulated. The increments were 10 (123 minus 113) and 6 (129 minus 123) mg/L, respectively. The analyst proceeded to Branch F.

Table 4

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L
0	100	0	100
0.1	113	25	113
0.2	123	50	123
0.3	129	75	129

To complete the table the following calculations were made based on the above formula:

First Addition

$$\frac{0.1}{50} \times 12{,}500 = \text{Total Standard Added (mg/L)} = 25 \text{ mg/L}$$

Second Addition

$$0.1 + 0.1 = 0.2 \text{ mL} = \text{Total Standard Added (mL)}$$

0.2 mL in the above formula gives 50 mg/L Total Standard Added.

Third Addition

$$0.1 + 0.1 + 0.1 = 0.3 \text{ mL} = \text{Total Standard Added (mL)}$$

0.3 mL in the above formula gives 75 mg/L Total Standard Added.

Branch D

Carefully check the instructions or directions for use of the procedure, making sure the proper techniques, reagents, titrant, sample volume, and digit multiplier were used. Verify there is no air or liquid, other than the titrant being used, in the delivery tube by ejecting several drops of solution. If the procedure in use is found to be in error, repeat Branch B using the correct procedure. If the procedure is found to be correct, proceed to Branch E.

Branch E

Check the performance of the reagents. This may be done easily by using a known standard solution to run the test or by obtaining a new fresh lot of the reagent. A list of known standard solutions is given in *Table 1* on page *20*. If it is determined reagents are defective, repeat Branch B with new reagents. If the reagents are proven in good condition, proceed with Branch H.

Branch F

Examples of non-uniform increments between standard additions on a sample are shown below in *Table 5*, *Table 6* and *Figure 2* on page 180. These plots illustrate the effect of interferences upon the standard addition and upon substances in the sample. The plots were made by graphing the Total Standard Added (mg/L) on the X axis and the Total Parameter Found (mg/L) on the Y axis as shown in *Figure 2* on page 180.

Table 5 Plot A

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	100	0	100
0.1	113	25	113
0.2	123	50	123
0.3	129	75	129

Table 6 Plot B

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	0	0	0
0.1	25	25	0
0.2	50	50	25
0.3	75	75	50

Both of these plots show that the four data points do not lie on a straight line. Plot A illustrates an interference which becomes progressively worse as the concentration of the standard increases. This type of interference is not common and may be caused by an error or malfunction of the procedure, reagents or apparatus. Perform Branch B to ensure that the supposed interference is present.

Plot B illustrates a common chemical interference which becomes less or even zero as the concentration of the standard increases. The plot shows the first standard addition was consumed by the interference and the remaining additions gave the correct increase of 25 mg/L for each additional 0.1 mL of standard added. The apparent interference in Plot B could be the result of an error made in the standard addition, and the analysis should be repeated with a fresh portion of sample.

The two examples illustrate chemical interferences which most certainly mean the result of the first analysis of the water sample was incorrect. When this type of interference is encountered, review the Interference section for the procedure for corrective steps. If this fails, the analyst should attempt to analyze the sample with an alternate method which, if possible, uses a different type of chemistry.

Branch G

Examples of uniform increments between standard additions on a sample are shown below in *Table 7* and *Table 8* on page 179. These plots illustrate the effect of interferences upon the standard addition and upon substances in the sample. The plots were made by graphing the Total Standard Added (mg/L) on the X axis and the Total Parameter Found (mg/L) on the Y axis as shown in *Figure 2* on page 180.

Table 7 Plot C

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	50	0	50
0.1	63	25	63
0.2	75	50	75
0.3	88	75	88

Plot C illustrates a common interference with a uniform effect upon the standard and the substances in the sample. The four data points form a straight line, but the titration increments between the additions is not correct. The straight line between the additions may be extrapolated back through the horizontal axis. The point of intersect of the line with the horizontal axis gives a more accurate estimate of the concentration of the substance in question for the sample. In the example, the first analysis of the sample gave 50 mg/L. The result located graphically (100 mg/L) using the accuracy check should be much closer to the correct result. Other interference effects may also be present, or interferences may not be consistent in all samples. Use of another method not subject to the interference, or elimination of the interference is preferred over extrapolation or use of the percent recovery calculation.

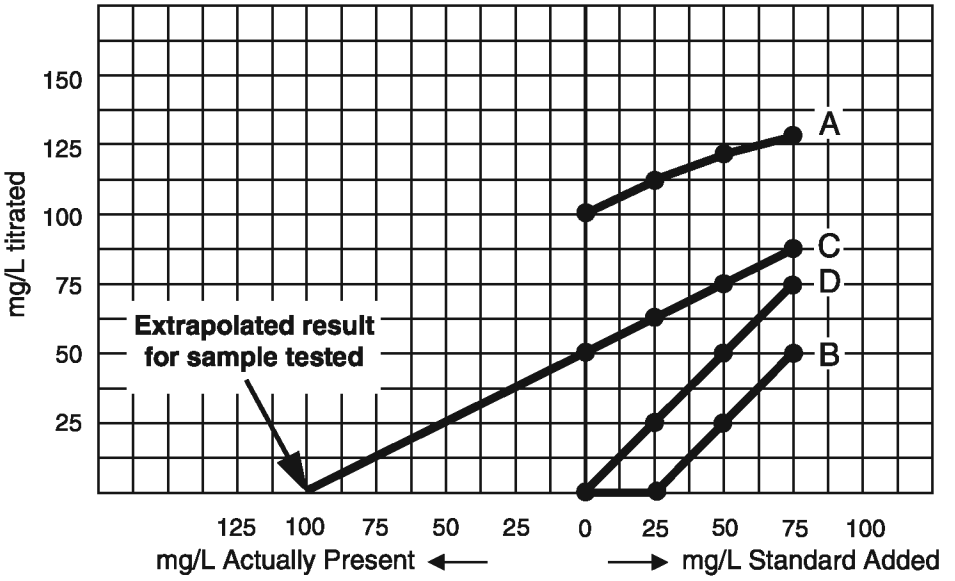
Apparent interferences also may be caused by errors in the method, a defect in the apparatus or standards. Before assuming the interference is chemical in nature, perform Branch B.

Table 8 Plot D

Total Standard Added (mL)	Total Number of Digits Used	Total Standard Added (mg/L)	Total Parameter Found (mg/L)
0	0	0	0
0.1	25	25	25
0.2	50	50	50
0.3	75	75	75

Plot D illustrates correct results but may hide a problem for the analyst. The increments found are uniform and the recovery of the standard was complete. The result of the first analysis was 0 mg/L and the plot graphs back through 0 mg/L. If interfering species are present, the interference may be sufficient to change the sample result but not sufficient to prevent the analyst from finding uniform increments and complete recovery of the additions. This would be an uncommon situation and results are probably correct unless unusual interferences are possible. Refer to the Interferences section in the specific procedure.

Figure 2
Multiple Standard Additions Graph



Branch H

Check operation of the apparatus used in the performance of the test. Verify the correct volumes of sample and standard were used. Check glassware used in the procedure, making sure that it is scrupulously cleaned. Dirty pipets and graduated cylinders are a source of contamination and will not deliver the correct volume. If a defect is found in the apparatus, repeat Branch B after repair or replacement of apparatus. If the apparatus is found to be in good working order, proceed with Branch I.

Branch I

After demonstrating that the procedure, reagents, and apparatus are correct and operating properly, the only possible cause for standard additions not functioning properly in deionized water is the standard used in performing the standard additions. Prepare or obtain a new set of standards and repeat Branch B.

Branch J
If the standard addition gave the correct result, the analyst must then determine if interfering substances are present. If interfering substances are not present, the result of the analysis prior to the standard addition is correct. If interfering substances are present, proceed to Branch C.

One of the greatest aids to the analyst is knowledge of the water sample's composition. An analyst need not know the exact composition of each sample but should be aware of potential interferences in the method of analysis to be used. When performing a particular method, the analyst should know if those interferences are present or not in order to have confidence in the accuracy of the results. Once the interferences are known, the Interference section of each procedure describes how to correct for many common interferences.

If the correct result is obtained with one standard addition when no interfering species are present, the chance of an error in sample results is very small. Possible sources of error not revealed include: sample quality, sample quantity (unless the sample and standard volume used is equal), and inconsistent end point determinations.

Call Hach Technical and Customer Support (1-800-227-4224) for additional help.

GENERAL INFORMATION

At Hach Company, customer service is an important part of every product we make.

With that in mind, we have compiled the following information for your convenience.

REPLACEMENT PARTS AND ACCESSORIES

REPLACEMENT PARTS FOR MODEL 16900 DIGITAL TITRATOR

Description	Unit	Cat. No.
Digital Titrator including delivery tubes, manual, and case	each	16900-01
Delivery Tubes, 180° hook	5/pkg	17205-00
Case	each	46602-00
Digital Titrator Manual	each	16900-08

HOW TO ORDER

By Telephone:

6:30 a.m. to 5:00 p.m. MST
Monday through Friday
(800) 227-HACH
(800-227-4224)
By FAX: (970) 669-2932

By Mail:

Hach Company
P.O. Box 389
Loveland, CO 80539-0389
U.S.A.

Ordering information by E-mail: orders@hach.com

Information Required

- Hach account number (if available)
- Your name and phone number
- Purchase order number
- Brief description or model number
- Billing address
- Shipping address
- Catalog number
- Quantity

Technical and Customer Service (U.S.A. only)

Hach Technical and Customer Service Department personnel are eager to answer questions about our products and their use. Specialists in analytical methods, they are happy to put their talents to work for you.
Call **1-800-227-4224** or E-mail **techhelp@hach.com**.

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Telephone: (970) 669-3050; FAX: (970) 669-2932

In Europe, the Middle East, or Mediterranean Africa:
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Dr. Bruno Lange GmbH
Willstätterstr. 11
D-40549 Düsseldorf
Germany
Telephone: +49/[0]211.52.88.0
Fax: +49/[0]211.52.88.231

REPAIR SERVICE

Authorization must be obtained from Hach Company before sending any items for repair. Please contact the HACH Service Center serving your location.

In the United States:
Hach Company
100 Dayton Avenue
Ames, Iowa 50010
(800) 227-4224 (U.S.A. only)
Telephone: (515) 232-2533
FAX: (515) 232-1276

In Canada:
Hach Sales & Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba
R3H 0X4
(800) 665-7635 (Canada only)
Telephone: (204) 632-5598
FAX: (204) 694-5134
E-mail: canada@hach.com

In Latin America, the Caribbean, the Far East, the Indian Subcontinent, Africa, Europe, or the Middle East:
Hach Company World Headquarters
P.O. Box 389
Loveland, Colorado, 80539-0389
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Telephone: (970) 669-3050
FAX: (970) 669-2932
E-mail: intl@hach.com

WARRANTY

Hach warrants most products against defective materials or workmanship for at least one year from the date of shipment; longer warranties may apply to some items.

HACH WARRANTS TO THE ORIGINAL BUYER THAT HACH PRODUCTS WILL CONFORM TO ANY EXPRESS WRITTEN WARRANTY GIVEN BY HACH TO THE BUYER. EXCEPT AS EXPRESSLY SET FORTH IN THE PRECEDING SENTENCE, HACH MAKES NO WARRANTY OF ANY KIND WHATSOEVER WITH RESPECT TO ANY PRODUCTS. HACH EXPRESSLY DISCLAIMS ANY WARRANTIES IMPLIED BY LAW, INCLUDING BUT NOT BINDING TO ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE.

LIMITATION OF REMEDIES: Hach shall, at its option, replace or repair nonconforming products or refund all amounts paid by the buyer. **THIS IS THE EXCLUSIVE REMEDY FOR ANY BREACH OF WARRANTY.**

LIMITATION OF DAMAGES: IN NO EVENT SHALL HACH BE LIABLE FOR ANY INCIDENTAL OR CONSEQUENTIAL DAMAGES OF ANY KIND FOR BREACH OF ANY WARRANTY, NEGLIGENCE, ON THE BASIS OF STRICT LIABILITY, OR OTHERWISE.

This warranty applies only to Hach products purchased and delivered in the United States.

Catalog descriptions, pictures and specification, although accurate to the best of our knowledge, are not a guarantee or warranty.

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HACH COMPANY
WORLD HEADQUARTERS
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Loveland, Colorado 80539-0389
Telephone: (970) 669-3050
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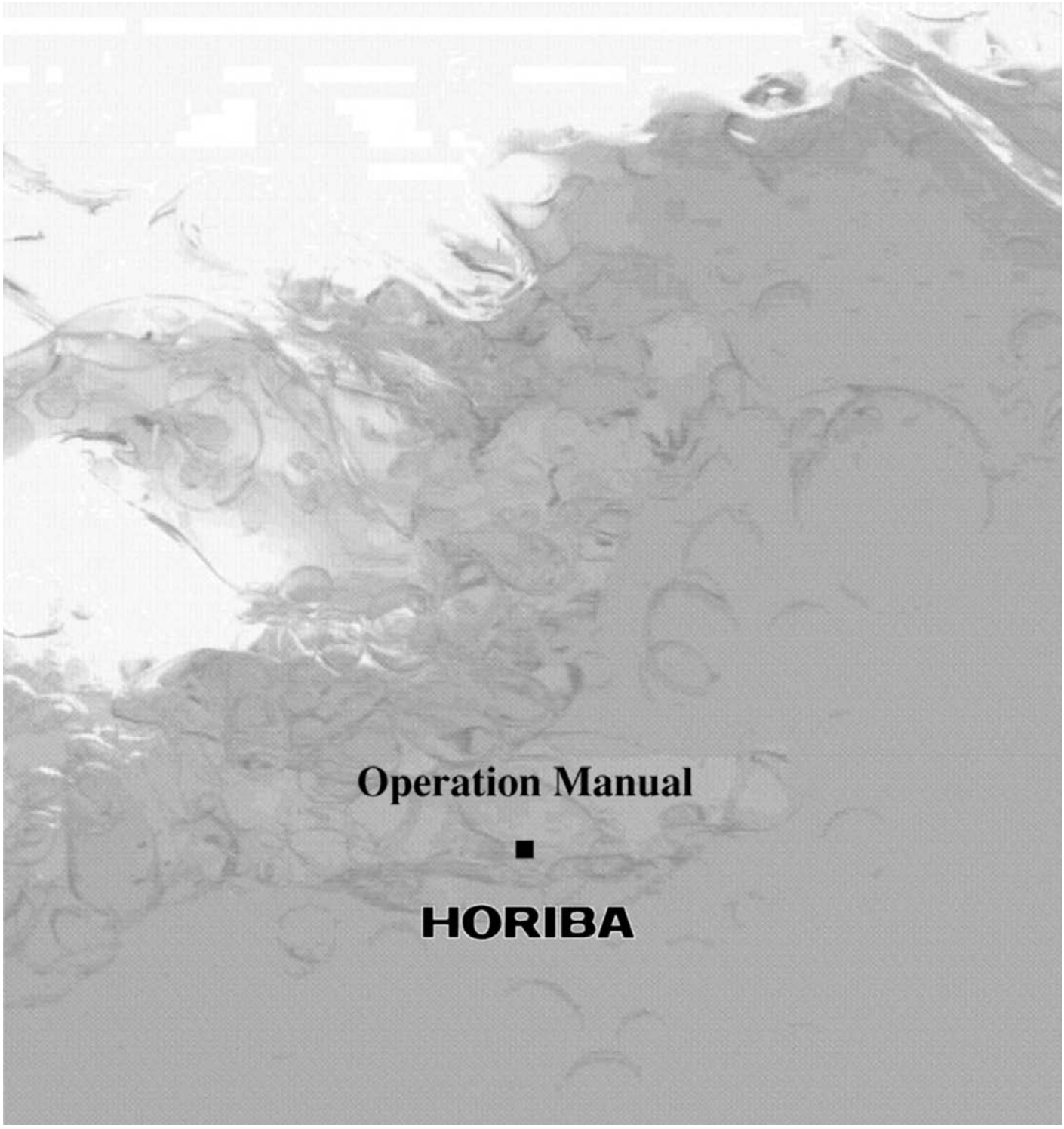
MULTI-PARAMETER WATER QUALITY MONITORING SYSTEM

U-20XD Series

U-22XD



Operation Manual

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HORIBA

HORIBA's Warranty and Responsibility

Your U-20XD series multi-parameter water quality monitoring system is covered by HORIBA's warranty for a period of one (1) year, under normal use. Although unlikely, if any trouble attributable to HORIBA should occur during this period, necessary exchange or repairs shall be conducted by HORIBA, free of charge.

The warranty does not cover the following:

- Any trouble or damage attributable to actions or conditions specifically mentioned in the operation manuals to be avoided
- Any trouble or damage attributable to use of the multi-parameter water quality monitoring system in ways or for purposes other than those described in the operation manuals
- If any repairs renovations, disassembly, etc. are performed on this multi-parameter water quality monitoring system by any party other than HORIBA or a party authorized by HORIBA
- Any alteration to the external appearance of this multi-parameter water quality monitoring system attributable to scratches, dirt, etc. occurring through normal use
- Wear and tear to parts, the exchange of accessories, or the use of any parts not specified by HORIBA

INSTALLATION ENVIRONMENT

This product is designed for the following environment:

→ Installation Categories II
→ Pollution degree 2

LIMITATION OF LIABILITY FOR DAMAGES

HORIBA will not accept responsibility for damage or malfunction that may occur as a result of operation or situation not recommended in this manual. HORIBA shall not be liable for Customer's incidental, consequential or special damages, or for lost profits or business interruption losses, in connection with the operation of the Manufactured Parts, CPU hardware, disk drives or Software.

CE MARKING

CE

U-20XD Series conforms with the following directive(s) and standard(s):

Directives:

the EMC Directive 89/336/EEC, in accordance with Article 10(1) of the Directive
the Low Voltage Directive 73/23/EEC

Standards:

[the EMC Directive] EN61326:1997+A1:1998
(EMISSION : Class B, IMMUNITY Category : General)
[the Low Voltage Directive] EN61010-1:1993 +A2:1995

FCC Warning

This equipment has been tested and found to comply with the limits for a Class A digital device, pursuant to part 15 of the FCC Rules. These limits are designed to provide reasonable protection against harmful interference when the equipment is operated in a commercial environment. This equipment generates, uses, and can radio frequency energy and, if not installed and used in accordance with the instruction manual, may cause harmful interference to radio communications. Operation of this equipment in a residential area is likely to cause harmful interference in which case the user will be required to correct the interference at his own expense.

Unauthorized reprinting or copying of this operation manual

No unauthorized reprinting or copying of all or part of this operation manual is allowed. The utmost care has been used in the preparation of this operation manual. If, however, you have any questions or notice any errors, please contact the HORIBA customer service printed on the back cover of this operation manual.

Preface

Thank you very much for purchasing HORIBA's "MULTI-PARAMETER WATER QUALITY MONITORING SYSTEM" U-20XD Series.

Compact and one-hand-held, our multi-parameter water quality monitoring system makes measurements about a large number of items simultaneously.

The instrument uses a large-sized LCD display and has a variety of functions through easy operation, being useful for use at sites where measurements are to be made.

The water-proof construction of the instrument is compliant with IP-67 of IEC 529, "Water-proof test on electrical and mechanical equipment and tools and protection grade against entry of solids." Please use the instrument by following the information in this Operation Manual to maintain the water-proof construction of the instrument.

IP-67 standards

- Keeping dust and grit out of the instrument
- Up to 5 °C difference between water and an instrument employed and no entry of water into. the inside of the instrument at a depth of I m for 30 minutes

This Operation Manual contains information on the basic way of handling the instrument, notes, etc. for the user. Be sure to read through the Operation Manual before use.

Symbols employed

The symbols employed herein have the following meanings:

⚠**WARNING** : Improper use can result in serious injury or even death.

⚠**CAUTION** : The improper use of the instrument may cause the following dangers:

- Danger of injury
- Danger of damage to the instrument, its peripherals, and data

: Description of what should never be done, or what is prohibited.

: Description of what should be done, or what should be followed.

Important : Explanation necessary for the proper operation of the instrument

Note : Explanation that is useful and necessary for handling the instrument

☞ : Refer to the item shown.

Symbols employed in screen description

The symbols and used in screen description have the following meanings:

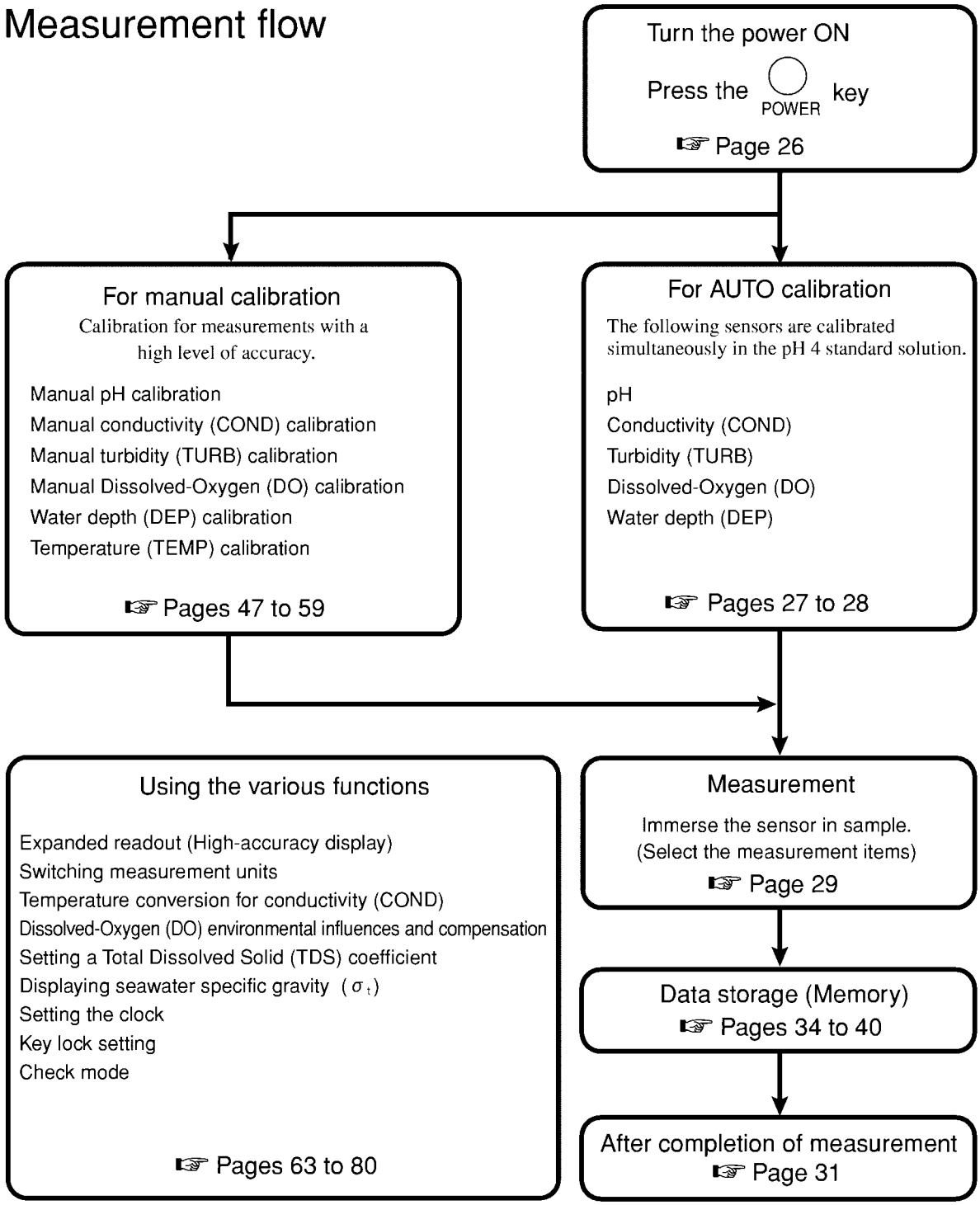
: The letters and numbers in this symbol are blinking on the screen.

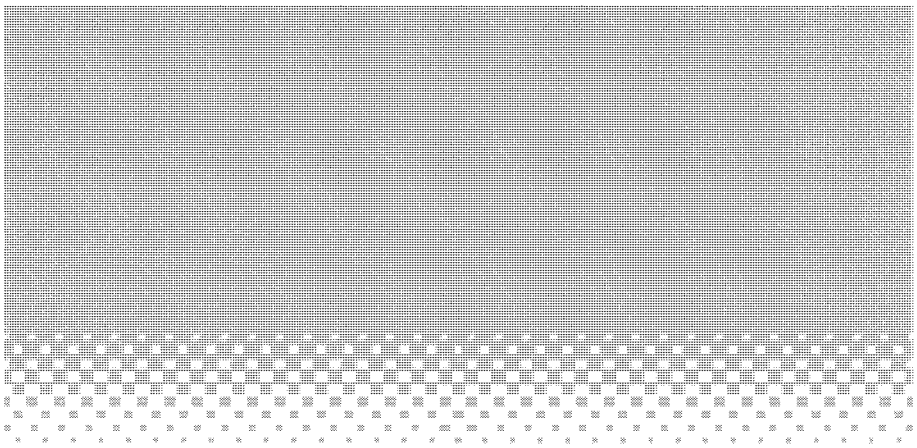
: The letters and numbers in this symbol are lighting up on the screen.

◉ CONTENTS ◉

◍ CONTENTS ◍

Measurement flow



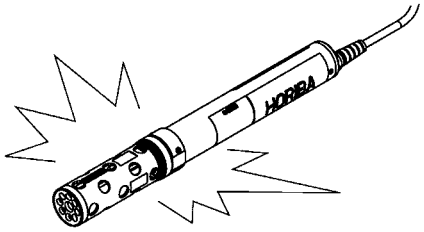


1. Introduction

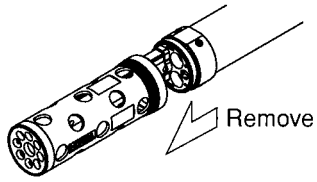
1.1 Notes on handling the instrument

Handling of sensor probe

Do not give a shock to the sensor probe.
The sensor will be damaged.

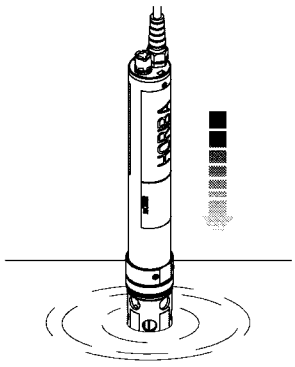


Do not remove the protection cover from the sensor probe to use.
Damage may occur to the sensor.



Slowly lower the sensor probe into the sample.

Dropping it from a height of 1m or more may cause damage to the sensor.
Do not immerse the sensor probe at the depth of exceeding 100 m.
The device can resist the hydraulic pressure at the dept up to 100 m.



- The protection cover may rust due to the environment in which it is used. The damage caused by this usage shall not be warranted by the manufacturer. Solve it with parts which users need to replace periodically.

⚠ WARNING

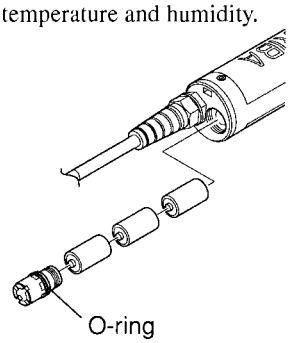
- Fix the sensor probe to the cable or the reel to use.
- In place with a large distance to the water level or with a rapid water flow, fix the sensor probe hook to a point except your body before use for safety purposes.
  Be careful not to let go off the sensor probe by mistake. Otherwise, the sensor probe together with the instrument will fall into the water or a sharp shock will occur to yourself while you are holding the instrument.

Replacing batteries and sensor of the sensor probe

Do not replace the sensor probe batteries and sensor in the atmosphere of high temperature and humidity.

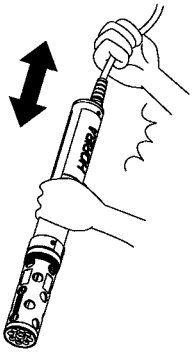
Put connector plugs into the sensor probe connectors with sensors off.

The sensor probe's battery cover is kept waterproof by the use of an O-ring. After checking that there are no foreign bodies adhering to the O-ring, apply silicon grease (included) to the face of the O-ring and close. Be sure to close it all the way to the indicated level. Do not close with the O-ring twisted or warped.

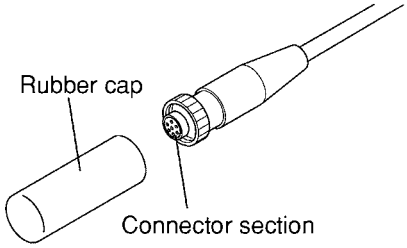


Handling of cable

Do not store the cable with its connector being greatly tensed or bent.
Do not submit the connector to strong shocks or the cable will snap.

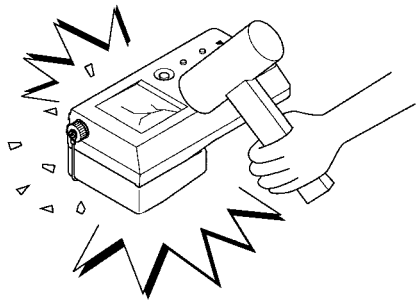


If sample waterdrops remain onto the connector section, metal part of the connector is likely to rust. When storing, wipe the area around the connector well and cover it with the rubber cap.

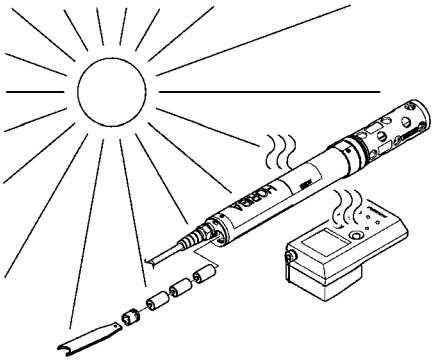


Handling of the instrument

Do not give a shock to or drop the sensor or instrument. The sensor or instrument will be damaged.

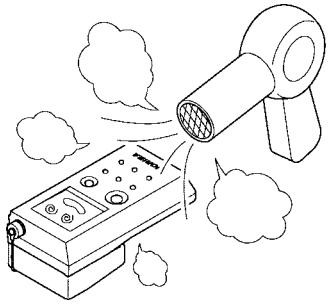


The display part includes LCD. Do not expose the instrument to ultraviolet rays for a long time. Otherwise, the LCD may deteriorate.

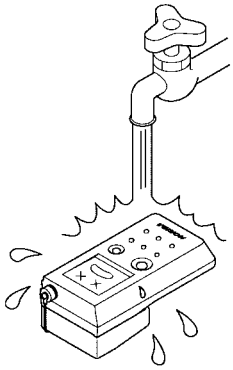


The instrument will be water-proof in construction (IP-67) when the sensor connector is connected to the instrument. However, if the instrument has been dropped into water or become wet, use a soft cloth to dry up the instrument.

Do not use a hair dryer to dry up the instrument.

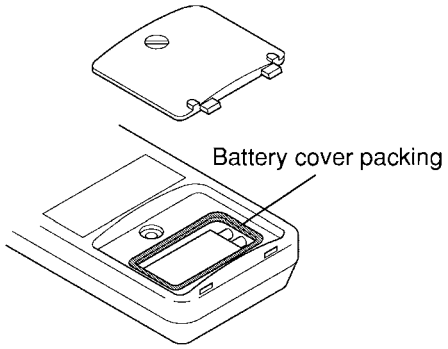


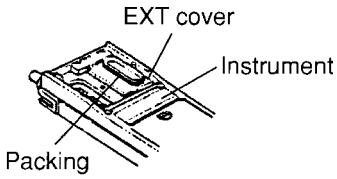
Do not wash directly the instrument using tap water from the faucet.



Note on replacing battery of the instrument and the section to which the EXT unit is attached

Waterproof function of the main unit is maintained by the packing of battery cover and EXT unit cover. Foreign matter on the packing can cause water to enter the instrument. Check for foreign matter on the packing before closing the battery cover and the EXT cover.
If the packing is twisted, do not close the battery cover and the EXT cover.





For a long use

We recommend that the packing be replaced once a year.
For battery cover packing replacement, contact your sales agent.

Note on place for use

- Avoid continuous measurement in water containing alcohol, organic solvent, strong acid, strong alkali or neutral detergent; otherwise the sensor surface will deteriorate.
- Do not use the instrument in the atmosphere with ambient temperatures below 0 °C (incl.) or above 55 °C (incl.).
- Avoid using the instrument in the condition exposed to strong vibrations or corrosive gases.
- Do not use the instrument near a source of strong electromagnetic field such as high-voltage cables and motors.

Batteries

The improper use of batteries may cause leaks and explosion.
Observe the followings:

- Set the batteries in place properly while paying attention to the plus (+) and minus (-) poles.
- Do not use both an old and new batteries or batteries of different types.
- Batteries for use in the instrument are not of the rechargeable type.
- Remove the batteries when not in use for a long time.
  In case of leaks, wipe off the solution in the battery case thoroughly and place new batteries in position.

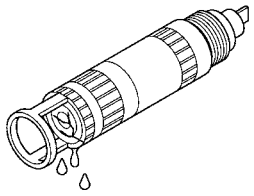
Handling the DO sensor

- In case of breakage of DO sensor diaphragm, replace DO sensor or replace just the diaphragm by using diaphragm replacement unit, without directly touching the internal solution.
- When removing the DO sensor from the sensor probe, make sure to install the short socket (included).

- Do not give a shock to the DO sensor. The sensor will be damaged.

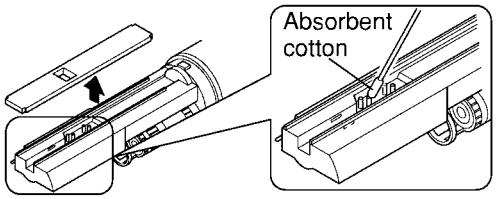
⚠CAUTION

- The DO sensor holds a strong-alkaline solution. Protect the eye and skin from the solution. If there is any solution in the eye or on the skin, immediately use sufficient water to wash off the solution. Consult a doctor as required.



Handling the COND/TURB unit

When cleaning the COND/TURB unit, use an absorbent cotton to avoid damage to the TURB cell.

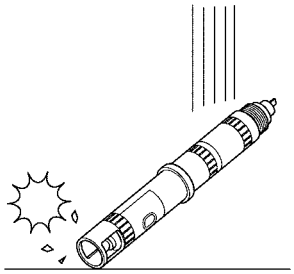


Handling the pH/ORP sensor

The pH/ORP sensor has a glass electrode at the end. Handle the sensor carefully to avoid a break in the glass electrode.

⚠CAUTION

- Be careful not to break the glass on the top of the sensor. Otherwise you may get hurt with a piece of glass.



Disposal

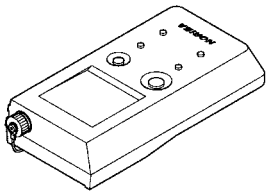
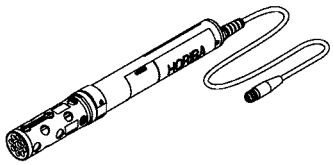
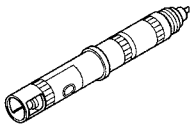
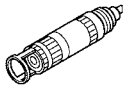
Dispose of this product as special waste, otherwise this may affect the environment.

Handling in transportation

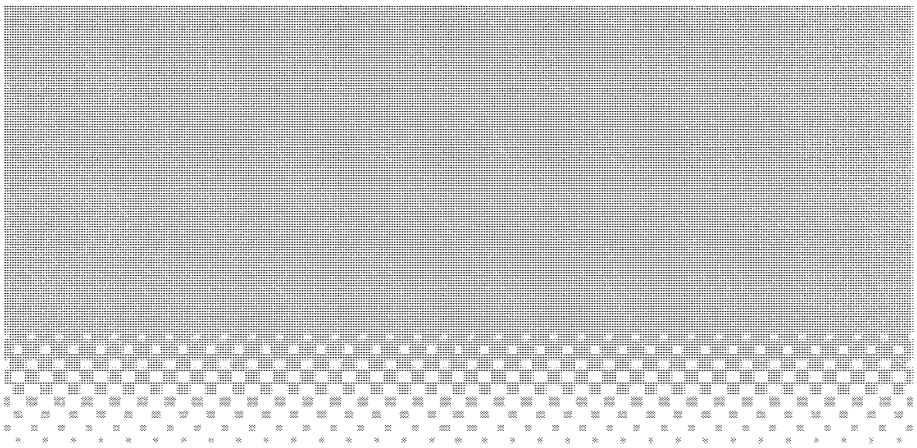
- When transporting this product as freight, use the carrying case to prevent damage.
- Remove the flow cell from the sensor probe in transportation.

1.2 Packing list

The U-20XD series is comprised of the following items.

Model	U-22XD
Meter (U-2000)	
Sensor probe	
Sensor	pH/ORP sensor 
	DO (Dissolved-Oxygen) Sensor 
Accessories	pH 4 standard solution (500 mL)
	pH internal solution (250 mL)
	pH syringe with needle
	Sensor spanner
	Calibration beaker
	Probe cap
	Grip holder
	Carrying case
	Manganese battery 6F22 (006P) (1 piece)
	Alkaline batteries LR03 (AAA) (3 pieces)
	Silicon grease
	Sensor O-ring (S8) (10 pieces)
	Sponge for probe cap (5pieces)
	Operation manual

- The included battery is for the monitor. Its life is not guaranteed.



2. Before Use

2.1 Introduction to the instrument

2.1.1 Measurement items

Components that can be measured with the U-20XD series models are as follows:

Model	U-22XD
Measurement items	
pH	○
Dissolved Oxygen (DO)	○
Conductivity (COND)	○
Salinity (SAL) [Conductivity conversion]	○
Total dissolved solids (TDS) [Conductivity conversion]	○
Specific gravity of seawater [Conductivity conversion]	○
Temperature (TEMP)	○
Turbidity (TURB)	○
Water depth (DEP)	○
Oxidation-Reduction Potential (ORP)	○

○ ..... Measurable

2.1.2 Introduction to functions of the instrument

Outline of the functions of the instrument is described below.

Feature	Function name	Page
Data obtained during measurement can be saved in the memory.	Manual data storage	Page 34
Data can be automatically saved in the memory at constant time intervals.	Auto data storage	Page 36
Saved data can be called.	DATA OUT	Page 41
The latest date of calibration and its details can be called.	Calibration history	Page 43
Enlarged display is available.	Expand readout	Page 63
Measurement units can be switched.	Switching measurement unit	Page 64

* Other functions possible in the check mode are available. (☞ Page 73)

2.1.3 Functions of expansion units

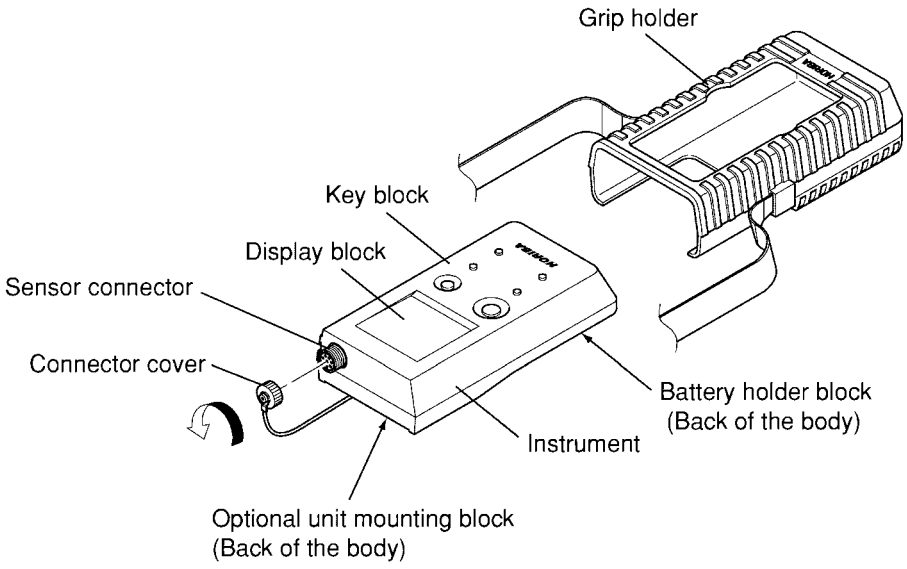
For the U-20XD series, use of expansion units allows communications with personal computers through RS-232C, the storage of G.P.S. data in the memory, and printer output, and commercial power supply.
Expansion units are available in the following two types:

Unit/name	Contents	Functions
U-2001	• Expansion adaptor	<RS-232C communications, G.P.S connection, and printer output>
Expansion adaptor	• Software for PC	The above functions cannot be used at the same time. One of the connectors for these three functions needs to be used.
U-2002	• System unit contain case	<RS-232C communications, G.P.S connection, printer output, battery power supply*>
System unit	• Software for PC	The above functions can be used at the same time.
	• G.P.S. unit	* A battery power supply can be used for measurements outdoors for 30 consecutive days.
	• Printer set	

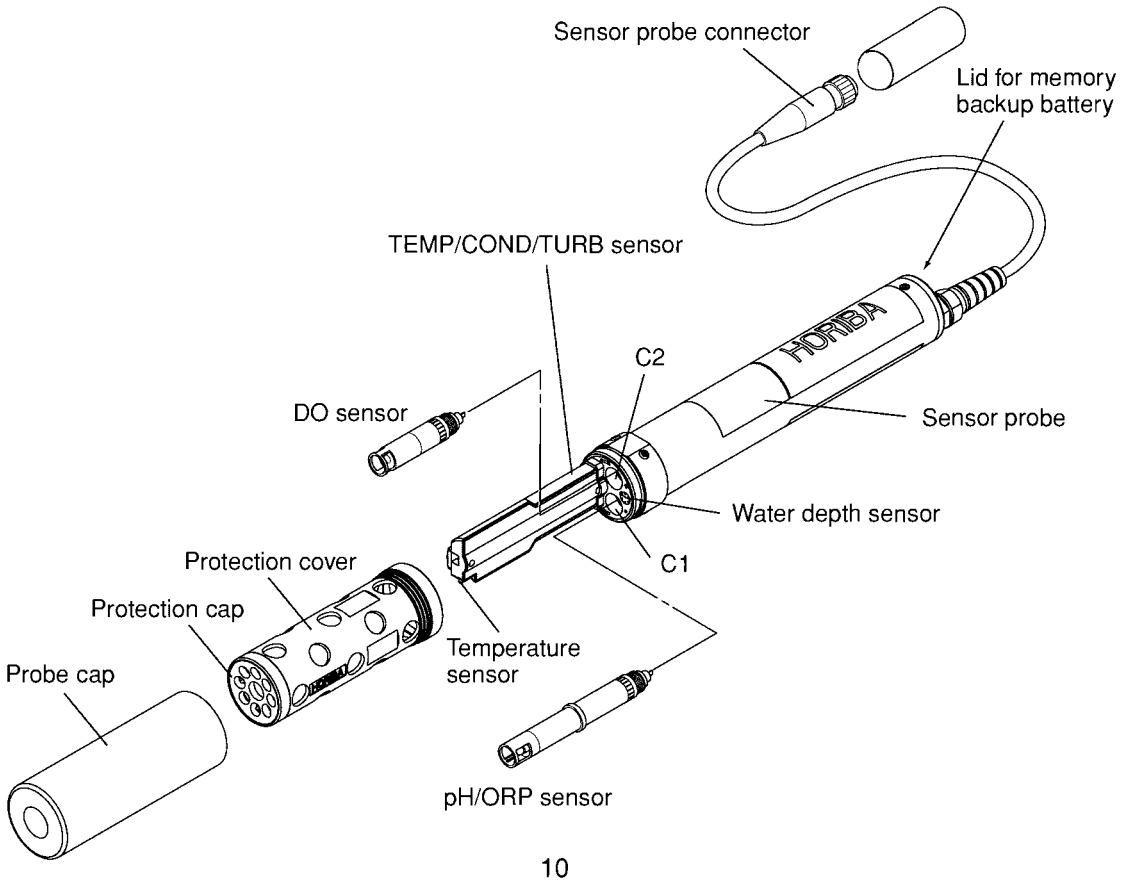
* U-2001 and U-2002 can operate on a commercial power supply through the use of an AC adapter (optional). However, the AC adapter cannot be used for the G.P.S. unit or printer set.

2.2 Names of the parts

2.2.1 Instrument name

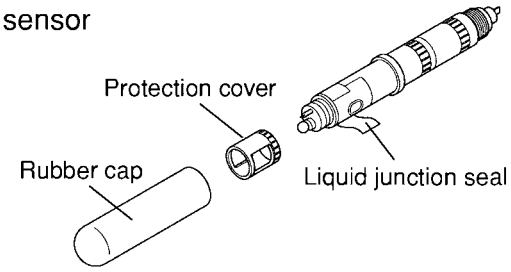


2.2.2 Sensor probe names

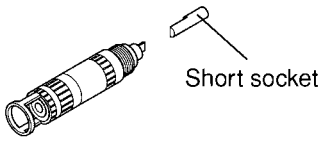


2.2.3 Sensor names

pH/ORP sensor



DO sensor



2.2.4 Use of carrying case

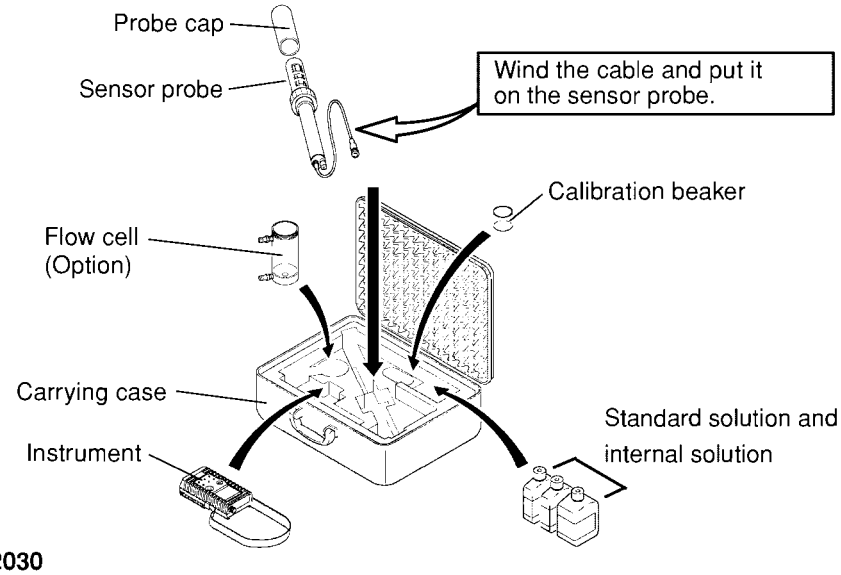
The carring case models W-2010 and W-2030 are applicable to store or transport U-22XD series.

Model	Applied to	Storage temperature	Material
W-2010	Cable length 10 m or less	-5 to 60℃	PP, ABS
W-2030	Cable length 30 m or more		

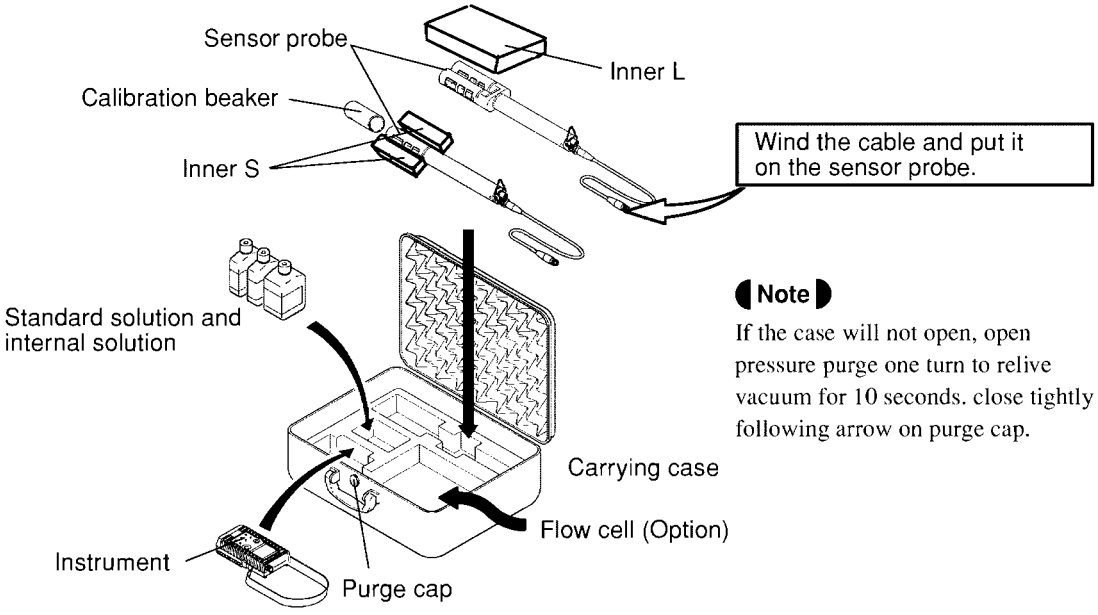
⚠CAUTION

- Do not drop or hit the carring case to protect the units against damage.
- When using the sensor probe with flow cell, separate them for strage.
- Be careful not to catch your finger, when fastening or releasing the laches.

• W-2010



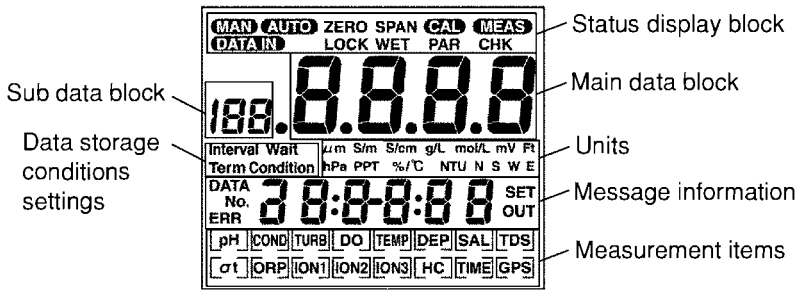
• W-2030



Note

If the case will not open, open pressure purge one turn to relive vacuum for 10 seconds. close tightly following arrow on purge cap.

2.2.5 Display



Status display block

MAN ..... On when the data memory and calibration settings are set to manual.
AUTO ..... On when the data memory and calibration settings are set to automatic.
DATA IN ..... On when the data memory operation and the data memorys operation settings are being performed. Blinking during calibration.
ZERO ..... On in the Zero calibration mode.
SPAN ..... On in the Span calibration mode.
CAL ..... On in the Calibration mode.
MEAS ..... On in the Measurement mode. (Measurements are being made when light up.)
LOCK ..... On when the keys are locked.
CHK ..... On when the instrument is in the check mode.

Sub data block

Display of the pH, Latitude (degree), Longitude (degree), Year and Check No.

Main data block

Display of Measurement data, Latitude (minute, 〔second〕), Longitude (minute, 〔second〕), and month and day.

Data storage conditions setting

Interval ..... On when a time interval is set for storage of data.
Wait ..... On when a time is set for waiting from the automatic data storage instruction until the start and during data processing through individual operations.
Term ..... On when a period is set for automatic data storage.

Units

Displays the units for measurement items.

Message information

Displays the stored data (data mode) and the data No. when the data is stored.
SET ..... Indicates that the instrument is in Set mode.

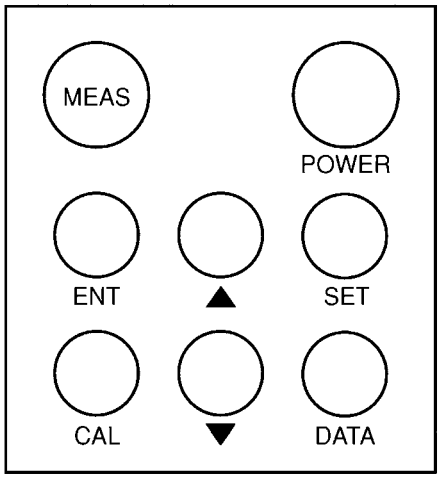
Measurement items

Displays the measurement items for the data in the main data block display. The display is read as follows.
Items without brackets (| |) ..... Items with the highlighted text will be stored in the data memory.
(☞ *Measurement item setting*, page 76)
Items with brackets (| |) ..... Displays the measurement items with data display.
(☞ *Measurement item setting*, page 76)

Note

- Because of the instrument's automatic power off function, the indication will disappear if the unit is not used for about 30 minutes. For operation of the unit and display of the indication, turn ON the instrument again.

2.2.6 Key names



POWER: Power key

Turns the instrument On and Off. Immediately after the power is switched on, the initial screen is displayed to indicate the status of the instrument.

MEAS: Measurement key

In the Measurement mode (MEAS is on), this key switches the measurement item. In addition, pressing the MEAS key returns you from the Setting, Calibration and Memory Call Up modes to the Measurement mode.

Note

- Regardless of which mode the instrument is in, it is always possible to return to the Measurement mode by pressing the MEAS key.

ENT: Enter key

In the Measurement mode (MEAS is on), pressing the ENT key stores the data in memory.
In the Calibration mode (CAL is on), pressing the ENT key performs calibration.
In the Setting mode, pressing the ENT key switches the setting and registers entered setting values.

CAL: Calibration key

Pressing the CAL key switches the instrument to the Calibration mode. If automatic data storage is in progress, it is aborted.

SET: Set key

Pressing the SET key switches the instrument from the Measurement mode to the Set mode. If the SET key is pressed on the "year, month, day, time" display screen, it switches the instrument to the Check mode.

DATA: DATA key

Pressing the DATA key switches the instrument to the Data mode.

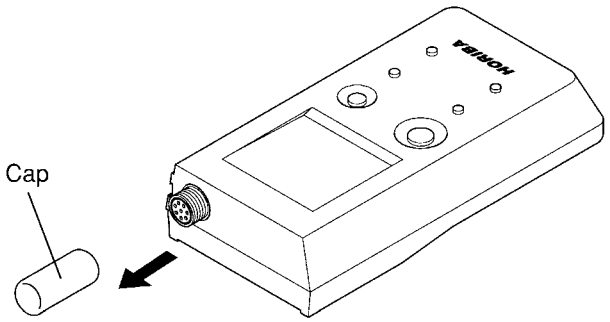
▲▼ : UP/DOWN keys

Use the UP/DOWN (▲▼) keys to set the calibration value in the Manual mode.

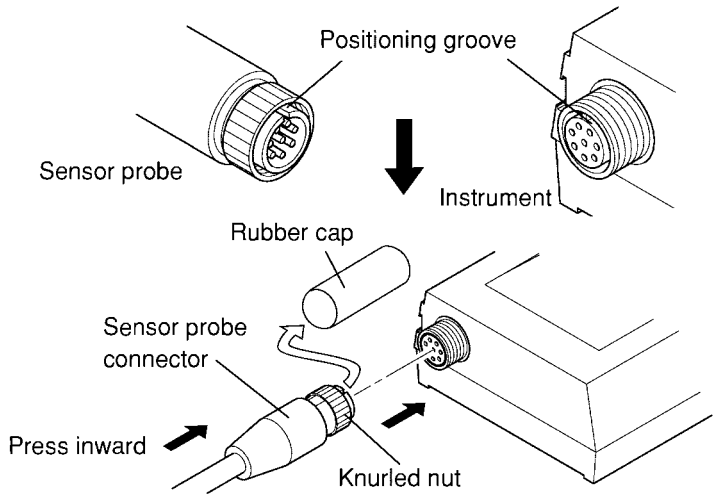
2.3 Setting up the U-20XD series models

2.3.1 Instrument and sensor probe connection

1. Remove the cap from the instrument's connector.



2. Align the positioning grooves of the instrument's connector and sensor probe connectors, and fit the connector of the sensor probe into the this other.



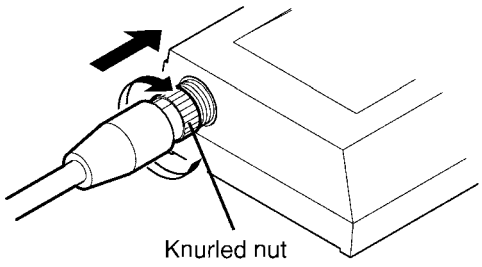
3. Press the sensor probe connector inward and turn. Tighten the connector until it will not turn any more.

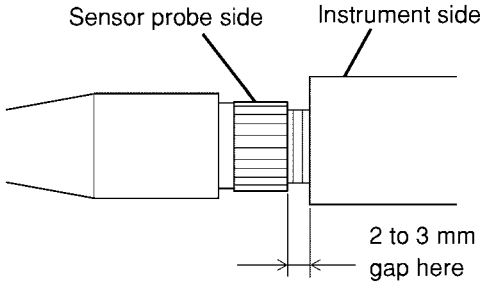
⚠CAUTION

- Turn the knurled nut with holding the knurled part. Otherwise, it will cause breaking of wire.

Important

- The connector cover or sensor probe connector should be connected to the instrument. Otherwise, the instrument will not be waterproof.
- Unless snugly attached, the instrument is not fully waterproof. When the sensor probe connector is tightened as far as it can go, a 2 to 3 mm gap is left between the instrument's connector and sensor probe connector.





Note

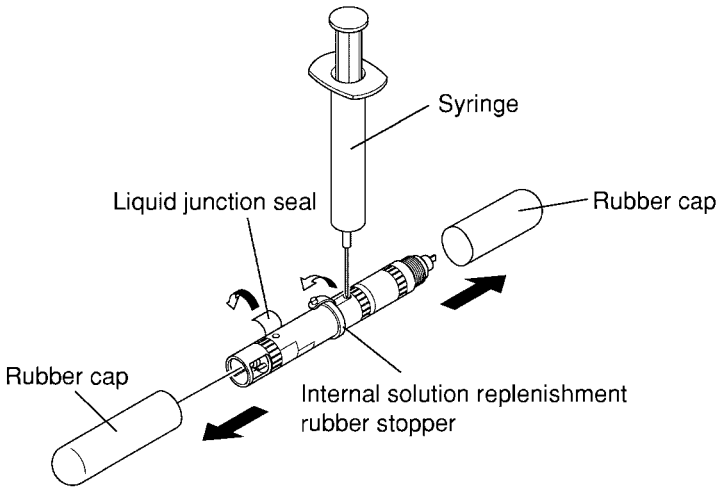
- Tighten the sensor probe connector until it will not turn any more.

2.3.2 Sensor installation

Connect the Dissolved Oxygen (DO) and pH/ORP sensors to the sensor probe.

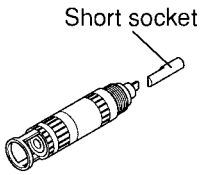
Preparing pH/ORP sensor

1. Remove the liquid junction seal and rubber caps.
2. Open the internal solution replenishment rubber stopper. Then use a syringe to take internal solution (#330).
   Air bubbles in the internal solution may impair the pressure compensation of the sensor. Allow as few air bubbles as possible to enter the inside solution.



Preparing DO sensor

1. Remove the short socket.



Important

- Provide the DO sensor with a short socket or connect the sensor to the sensor probe for storage. Otherwise, the sensor may have a shorter life or stable instructions may not be obtained.
- The short socket is used when storing. Do not throw it away.

Resetting the DO sensor when storing without having installed the short socket.

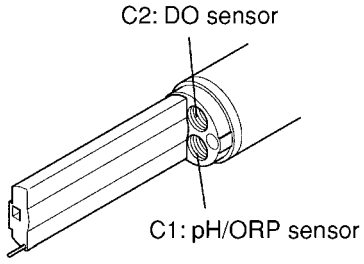
When leaving the DO sensor unattended for a brief period (1 or 2 days) without the short socket, the DO sensor can be reset by connecting it to the short socket or the probe. However, an amount of time corresponding to the period it was left unattended is necessary. If left unattended without being connected to the short socket or the probe for a long period (1 month), it cannot be reset.

Where to attach

1. The hole on the sensor probe in which each sensor is attached is determined by the type of sensor. Check the type of sensor and the assigned hole before attaching anything.

Important

- Installing the sensor in the wrong hole will damage both the sensor and sensor probe.

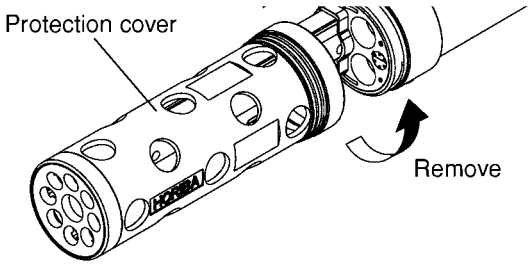


Installation procedure

Important

- With the U-22XD sensor probe install the DO sensor first and then the pH/ORP sensor.
- We recommend that the O-ring of the sensor be replaced with a new one each time the sensor is removed.

1. Remove the probe cap and remove the protection cover from the sensor probe.



When the protection cover's screws are firmly fixed in place and cannot be removed by hand, place a spanner on the protection cover and the surface of the cover guide and remove.

Do not try to remove the protection cover by hitting it or submitting it to shocks.

2. Apply silicon grease to the DO sensor's O-ring.

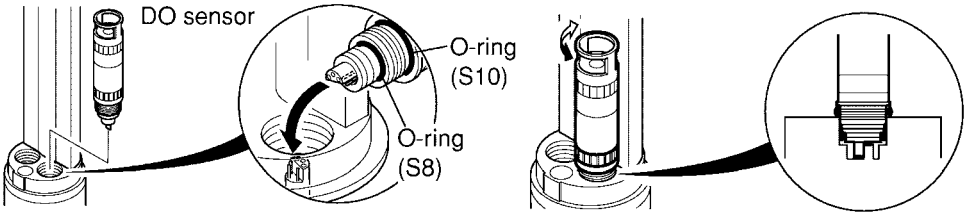
Make sure that no silicon grease gets on the connector.

3. Fit the DO sensor inside the sensor probe hole, being careful to align the shape of the connectors.

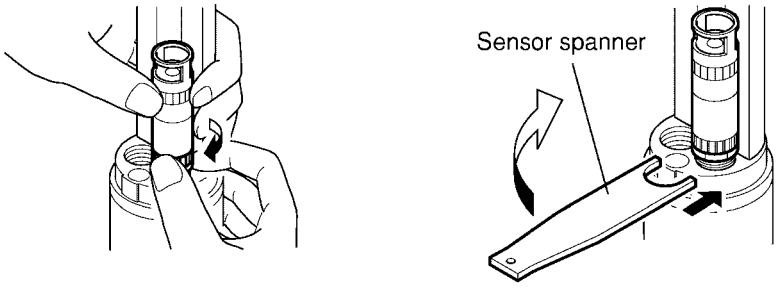
- Make sure that the O-ring is not scratched or twisted. Leakage will cause failures.
- Remove the DO sensor connected to the probe and, when reconnecting them, replace the O-ring (S8) on the smaller end of the DO sensor with a new O-ring.

Important

- Press the sensor slightly inward and try turning to check the fit. The sensor cannot be turned if inserted properly.



4. Turn the screw 2 or 3 turns by hand and then fully tighten with the sensor spanner.

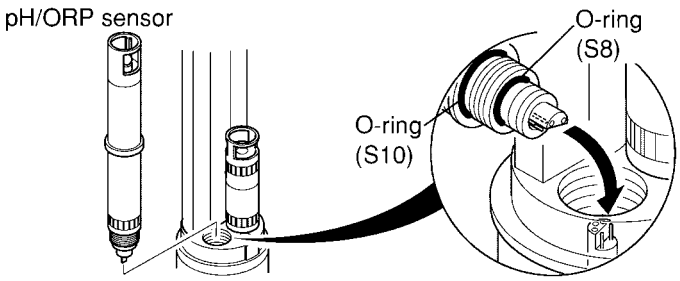


5. Apply silicon grease to the pH/ORP sensor's O-ring.

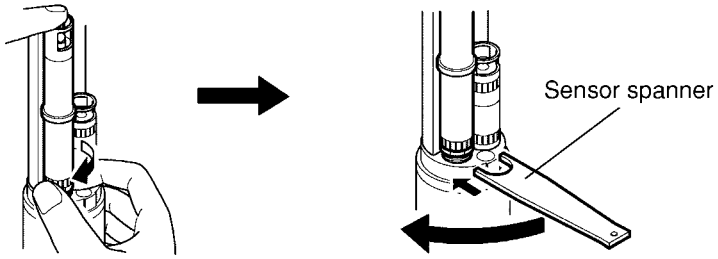
Make sure not to get silicon grease on the connector.

6. Fit the pH/ORP sensor inside the sensor probe hole, being careful to align the shape of connectors.

- Make sure that the O-ring is not scratched or twisted. Leakage will cause failures.
- Remove the pH/ORP sensor connected to the probe and, when reconnecting them, replace the O-ring (S8) on the smaller end of the pH/ORP sensor with a new O-ring.



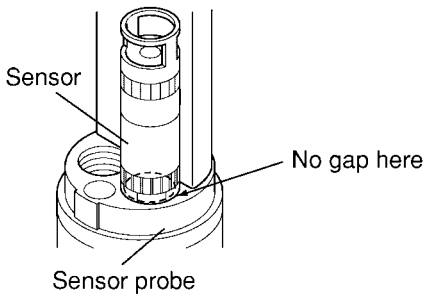
7. Holding the top of the pH/ORP sensor with your finger, turn the screw 2 or 3 turns by hand and then fully tighten with the sensor spanner.



⚠CAUTION

- Unless snugly attached, the sensor is not fully waterproof. The sensor is snugly fit inside the sensor probe when tightened as far as it will go.

Example for DO sensor



8. Attach the removed protection cover to the sensor probe as it was.

Important

- Before attaching each sensor to the sensor probe, do not soak the connector block in water.
- Be careful not to contaminate or wet the sensor probe or sensor connector.

Fasten the guard cover with your hand until it touches the end surface. If improperly fastened, it will slacken and, when storing the instrument, there will be a lack of humidity control. Fastening by hand is enough, do not use a spanner or other tool to fasten or the screws may break.

2.3.3 Installation and replacement of the battery

The U-20XD series is shipped from the factory with the battery packed separately.
When using the instrument for the first time or replacing the battery, perform the following procedure:

Type of battery:

Instrument (U-2000) ..... Alkaline battery 6LR61 (Manganese battery 6F22 [006P])
1 piece. (Battery for instrument operation)
Sensor probe ..... Alkaline batteries LR03 [AAA] (Manganese battery [R03])
3 pieces. (Battery for memory backup)

Notes on handling the battery

The improper use of battteries may cause leaks and explosion.
Observe the followings:

- Set the batteries in place properly while paying attention to the plus (+) and minus (-) poles.
- Do not use both an old and new batteries at a time or batteries of different types.
- Battteries for use in the instrument are not of the rechargeable type.
- Remove the batteries when not in use for a long.
  In case of leaks, wipe off the solution in the battery case thoroughly and place new battteries in position.

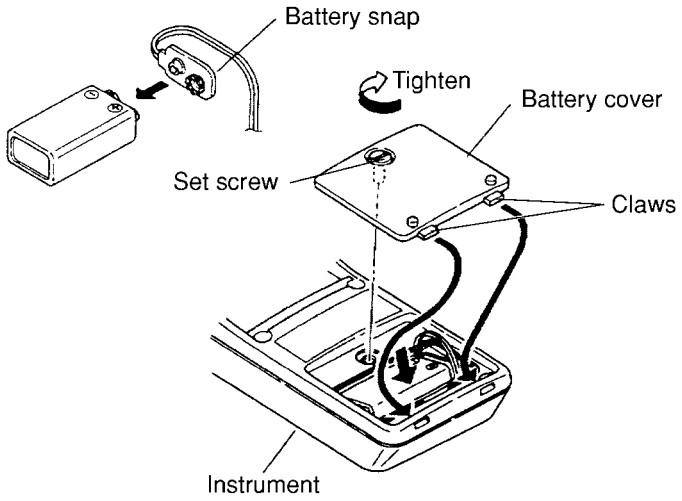
Note

- The battery originally attached to your unit is for monitor and the service life of the battery cannot be guaranteed.

Instrument (U-2000)

1. Loosen the set-screw on the battery cover and remove the cover.
2. Remove any old battery.
3. Fit the battery snaps to a new battery and insert the battery assembly into the instrument.
4. Insert the claws on the battery cover into the grooves in the instrument. Then tighten the set screw.

   The battery snap may be loose for some batteries. In such a case use radio pliers and tighten the metal snap fittings.

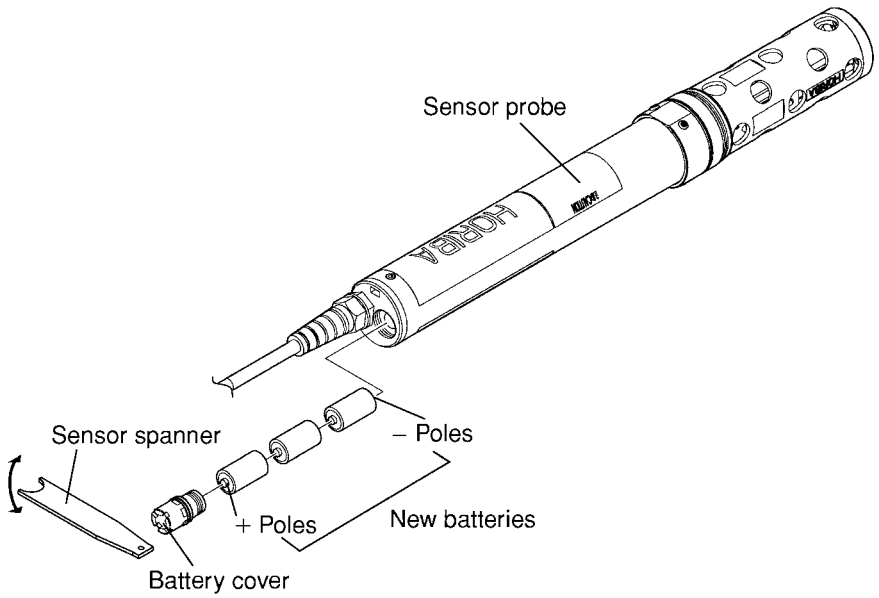


Important

- When removing the battery snap, do not pull it too strongly.

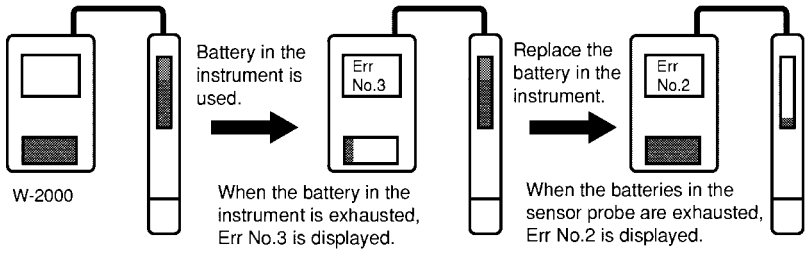
Sensor probe (for memory back up)

1. Remove the battery cover using a sensor spanner or a suitable object.
2. Remove any old batteries.
3. Insert new batteries making sure that the plus (+) and minus (-) poles match the terminals correctly.
4. To keep the sensor probe water-resistant, use a chip spanner as illustrated below and tighten the battery cover until the cover does not turn any more.



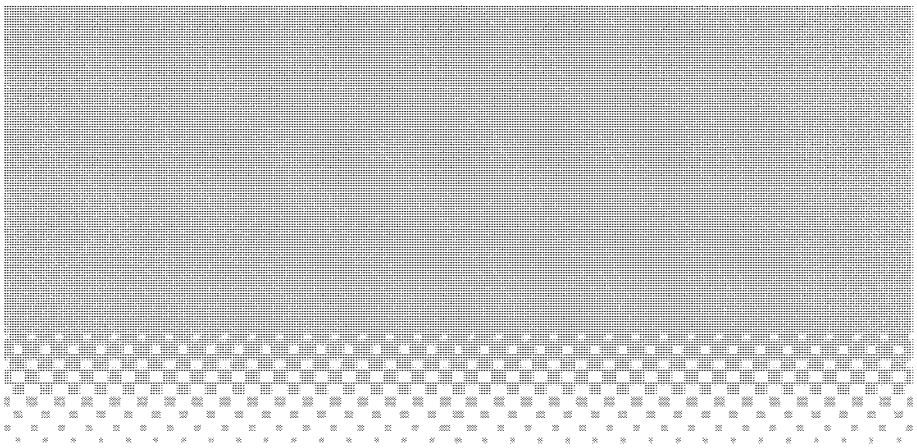
⚠ CAUTION

- When replacing the batteries of the sensor probe, be sure to connect the sensor probe to the instrument. Otherwise, the memory will be reset and all the data saved in the memory will disappear.
- When the sensor probe is connected to the instrument, battery in the instrument is consumed.



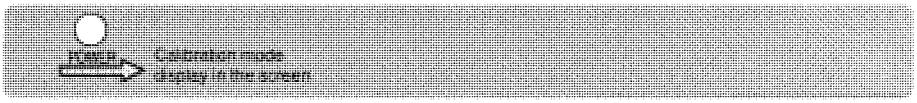
Note

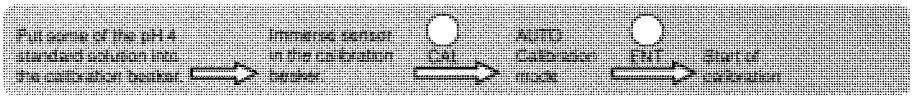
- The battery on the main unit is used up first allowing up to 30 hours use at room temperature. (When using alkaline batteries.)
- Life is reduced by approximately one half when manganese batteries are used.



3. Basic operation

The pH, conductivity (COND), turbidity (TURB), dissolved-oxygen (DO) and water depth (DEP) sensors can be calibrated automatically. Upon completion of this chapter, even beginners should be able to make measurements easily.



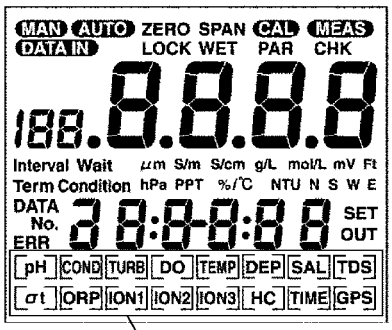


3.1 Key operations and mode switching

Measuring items and displays which are switched with the MEAS key

The items measurable with individual models are displayed. The items selected with the MEAS key will be indicated with [ ].

Example: In the pH Measurement mode: [pH]



Display block

The symbols displayed and their meanings are as follows:

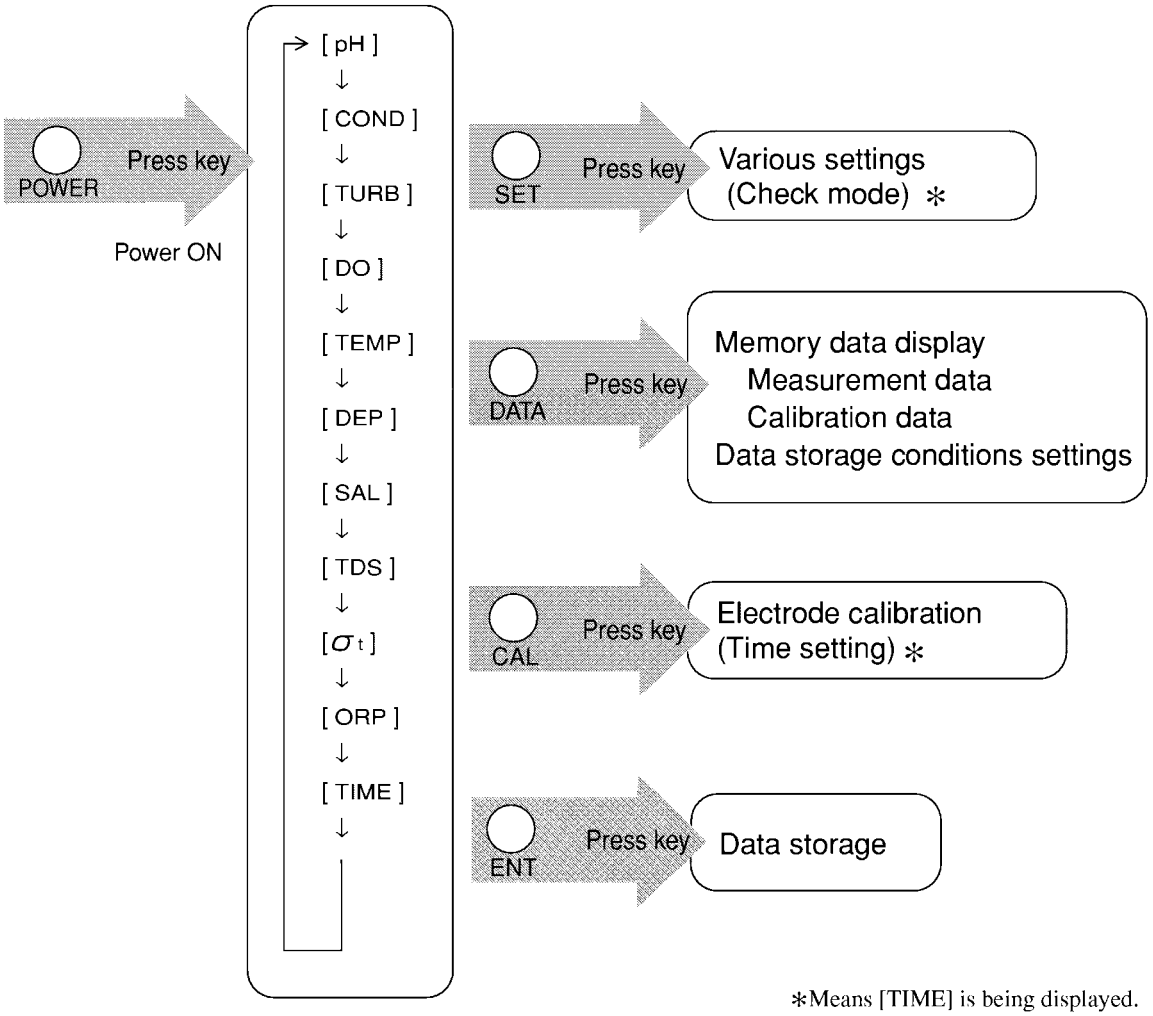
pH ..... pH
COND ..... Conductivity
TURB ..... Turbidity
DO ..... Dissolved-Oxygen
TEMP ..... Temperature
DEP ..... Depth
SAL ..... Salinity
TDS ..... Total dissolved solids
σ_t ..... Specific gravity of seawater
ORP ..... Oxidation-reduction potential
TIME ..... Display of date and time
GPS ..... G.P.S. (Global Positioning System) for imformation of position

Note

- [GPS] lights up when the optional G.P.S. sensor has been connected to the instrument and position information is received from the G.P.S. sensor during the measurement. For more information, refer to the instruction manual for the expansion units.

Measurement mode

MEAS When the MEAS key is pressed, the next measurement item appears.



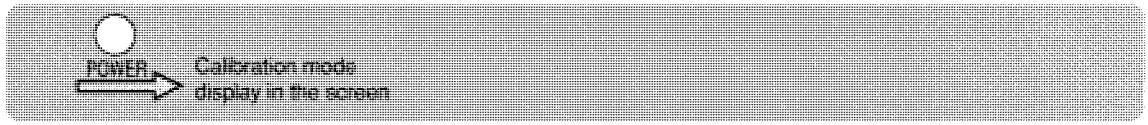
∗Means [TIME] is being displayed.

Note

- *"Measurement item setting"* on page 76 explains how to set the display so items are not displayed.

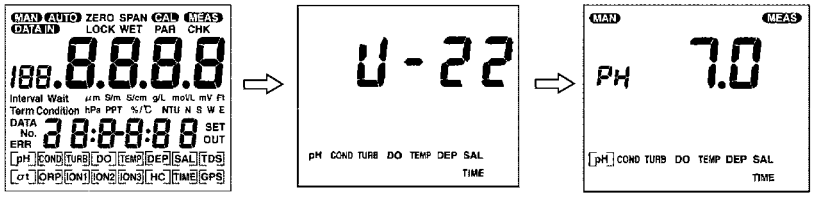
3.2 Operation procedure

3.2.1 Power ON

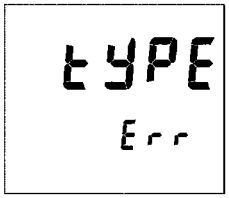


1. Press the **POWER** key.

The display will change in the order of All segment display → Sensor detector display → pH Measurement mode.



With the sensor probe is not connected,



is displayed.

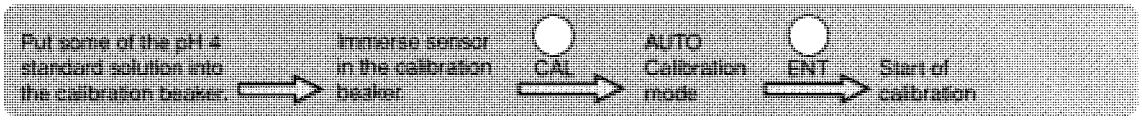
Before turning ON the instrument, connect the sensor probe properly.

3.2.2 AUTO calibration method

To obtain correct measurement, it is necessary to calibrate the sensor using the standard solution before performing measurement.
Previous calibration records shown in calibration log.
(☞ 4.3.2 *Calling up The calibration log*, page 43.)

Note

- In the AUTO calibration mode, the pH, COND, and TURB sensors are calibrated in the pH 4 standard solution, and the DO and DEP sensors in the atmosphere simultaneously.
  Calibrate contents at 25°C are as follows:
  pH: set at 4.01 (zero calibration) and the Span is the adjustment value at the factory when shipping.
  COND: 0.449 S/m (Span calibration), the Zero is the adjustment value at the factory when shipping.
  TURB: 0 NTU (zero calibration), the Span is the adjustment value at the factory when shipping.
  DO: 8.52 mg/L (Span calibration), the Zero is the adjustment value at the factory when shipping.
  DEP: 0 m (Zero calibration), the Span is the adjustment value at the factory when shipping.
- Values may be unstable if there is temperature fluctuation. Calibrate after waiting for about an hour.

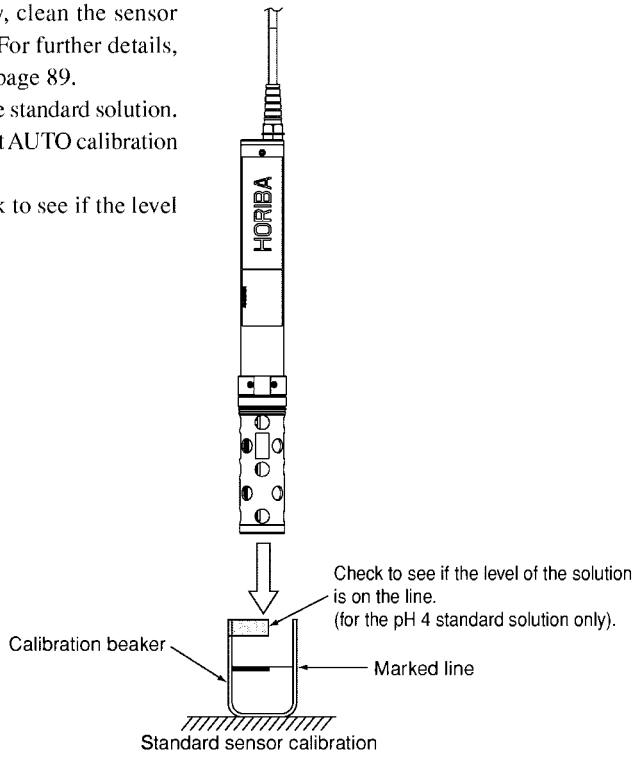


Calibrate using the following procedure.

1. Wash the sensor in distilled water a few times and put some of the pH 4 standard solution into the calibration beaker to the marked line. Then immerse the sensor in it.

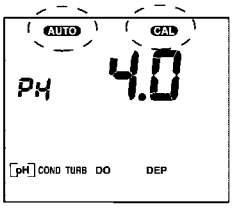
Important

- To carry out calibration for turbidity accurately, clean the sensor surface that will be soaked in standard solution. For further details, see "Troubleshooting for the TURB sensor" on page 89.
- Use the "100-4" manufactured by HORIBA for the standard solution. With other standard solutions, you cannot carry out AUTO calibration correctly.
- Use the label on the calibration beaker and check to see if the level of the calibration solution is on the label line.



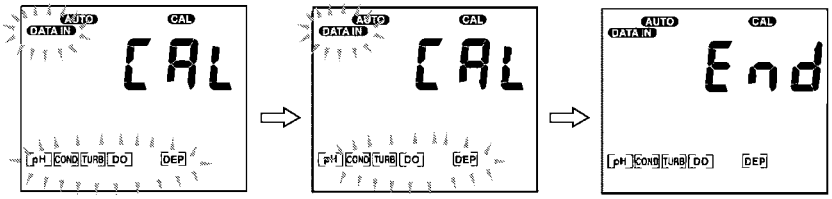
2. Press the **CAL** key in one of the Measurement modes pH, COND, TURB, DO and DEP.

AUTO and **CAL** appear and the instrument enters the AUTO Calibration mode.



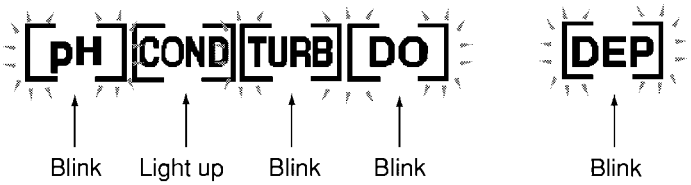
3. Press the **ENT** key to start AUTO Calibration.

Upon completion of all of the pH, COND, TURB, DO, and DEP modes, **End** will be displayed.
During calibration, **DATA IN** and [ ] for the selected measurement item blink. [ ] light up for the item of which calibration is finished.



With DATA IN is blinking
To stop calibrating the sensor .... press the CAL key.
To establish the calibration ..... press the ENT key.

Example: When COND calibration is finished:
[ ] for [COND] stops blinking and light up steadily.



Note

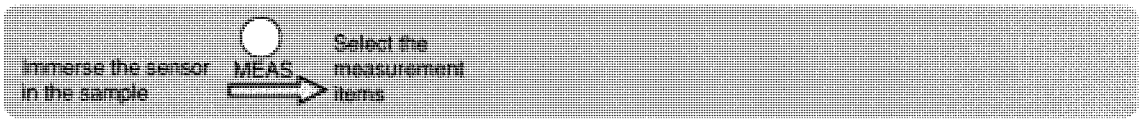
- [ ] continues to blink because calibration is not performed for the item for which an error has happened. If two or more errors happen, an error with a smaller number appears. (See pages 85 to 88 for these errors and ways to solve them.) These calibration errors disappear when the sensor is calibrated properly again, or when the instrument is turned ON again.
- Calibration should be performed for maximum three minutes. When the indications become stable, calibration should be finished.

4. Press the **MEAS** key to return to the Measurement mode.

Important

- Neutralize any basic pH 4 fluids before disposal.

3.2.3 Measurement



1. Immerse the sensor in the sample.

2. Select the measurement item.

Use the MEAS key to switch measurement items in the following order:

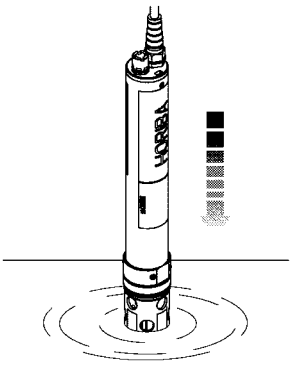
pH → COND → TURB → DO → TEMP → DEP → SAL → TDS → σ_t → ORP → TIME → then back to pH.

Note

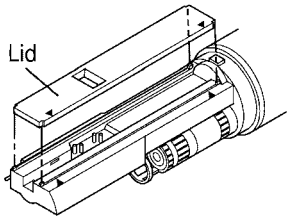
- [GPS] lights up when the optional G.P.S. sensor is connected to the instrument and position information is received from the G.P.S. sensor.
- The above measurement items can be changed by setting ""*Measurement item setting*" described on page 76.

Important

- When immersing the sensor probe in the sample, slowly lower the sensor probe into the sample.
- Dropping it from a height of 1m or more may cause damage to the sensor.



- Don't remove the COND/TURB lid during calibration or measurement.
- Attach the lid to the cell with fitting four corners and facing ▲ marks each other.



- Perform AUTO calibration after attaching the lid again, when the lid has been removed for the cleaning. A slight difference of the fitting position of the lid causes the difference of the indicated value for turbidity.
- Contacting with a different kind of metal, protection cover of the sensor probe may cause an error in measurement. Be careful not to let protection cover touch with any metal in measurement.

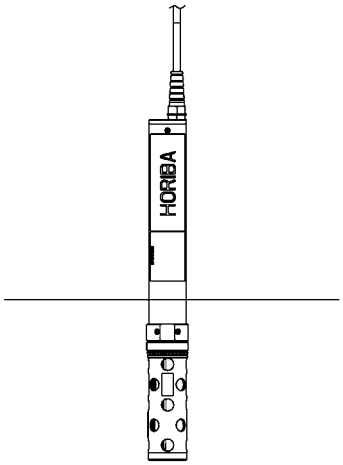
Two useful uses of the U-20XD Series models

Making measurements

1. Manually storing the measurement data after checking the indication becomes stable

Example: After switching measurement items with the MEAS key, you can then store the measurement data after checking the indication becomes stable.

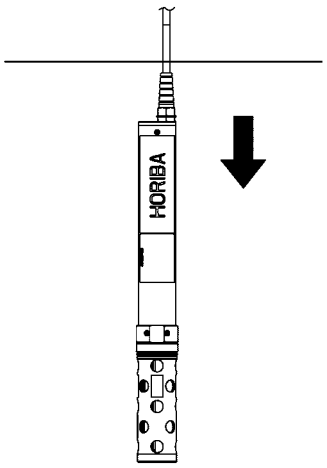
(☞ 4.1 *Manual storage of data while monitoring the measurement data*, page 34.)



2. Storing data

Example: Data can be stored continuously at constant intervals from the start of the automatic data storage. This function is useful in obtaining data in depth direction and in storing data continuously.

(☞ 4.2 *Automatic data storage*, page 36.)



Notes in obtaining data on depth

- When the instrument is placed at a depth of 100 m or more, the instrument may be broken.

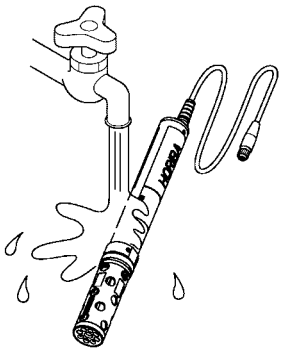
Notes for reliable measurements

- Any sensor contamination may affect measurements. Use the AUTO calibration mode to check for contamination on sensors about once a week for measurements.

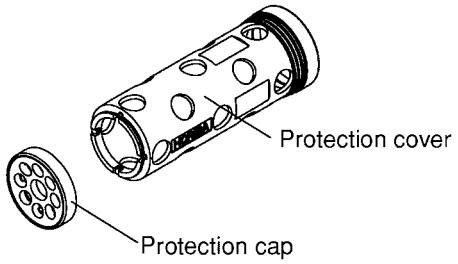
3.2.4 After completion of measurement

1. Turn the power to the instrument off.

2. Use tap water to completely wash off the sample on the sensor and then wipe waterdrops.



Remove the protection cover once and completely wash out with tap water the left over sample on the screws. Reinstall the cover after having wiped off the drops of water. If there is any sample (especially sea water) left over on the screws, rust may form which may prevent the protection cover from being removed. (☞ Installation procedure, page 18.)
Depending on the level of contamination, remove the rubber protection cap from the tip of the protection cover and wash out with tap water. Reinstall it after wiping off the drops of water.



3. Pour about 20 mL (about 2 cm from the bottom)of pure water in the probe cap and install it on the sensor probe. Place the rubber cap on the connector and store the instrument in the carrying case. (☞ 2.2.2 Sensor probe names, page 10.)

When storing with the ph/ORP and DO sensors attached to the probe, make sure to install the probe cap after having poured pure water into it.
Letting the ph/ORP and DO sensors get dry may cause deterioration of the instrument's performance. Should the sponge inside the probe cap be contaminated, replace it with a clean sponge (included).

Now you have read the description for performing measurements. For further information on how to use the instrument, refer to the chapters hereafter.

MEMO

4. Using the data memory function

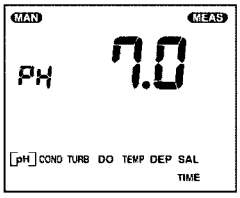
The data memory function can be used to store manualy measurement values with associated data numbers and to store automatically measurement values at fixed intervals (data logger).

4.1 Manual storage of data while monitoring the measurement data

Make sure MAN is displayed on the measurement screen. → ENT → Start data storage.

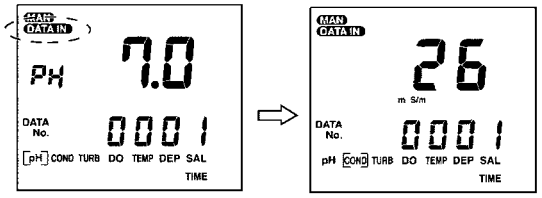
1. Make sure that **MAN** is displayed on the Measurement mode.

If **AUTO** is displayed, switch to **MAN** display.
(☞ page 35, Switch to **MAN** display on the measurement mode)



2. Press the **ENT** key.

Data storage starts, **DATA IN** and the data No. are displayed on the screen, and the measured value to be stored and the measurement item are displayed in order at approximately 0.5 second intervals.



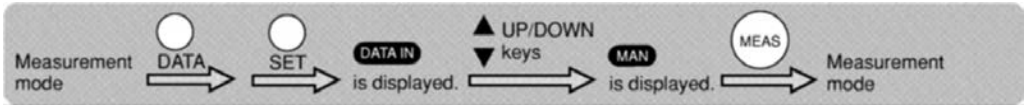
All measurement items and times are stored in sequence.

After the data is stored in memory, the screen returns to the original Measurement mode.

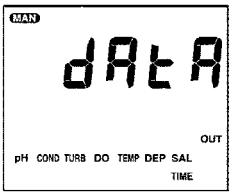
Note

- Up to 2880 sets of data can be stored in the memory.
  When 2880 sets of data have been stored in the memory, ERR 9 appears and no more data can be stored. In this case, "*Data memory clear*" while referring to page 78, and you can store new data in the memory.

When AUTO is displayed
Switch to MAN display on the measurement mode

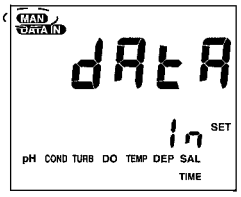


1. Press the **DATA** key in the Measurement mode.



2. Press the **SET** key.
DATA IN is displayed.

3. Press the **UP/DOWN** (▲ ▼) keys to display MAN.

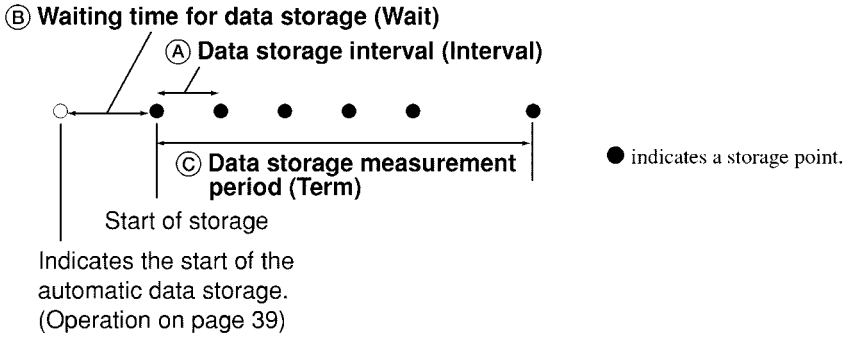


4. Press the **MEAS** key to return to the Measurement mode.

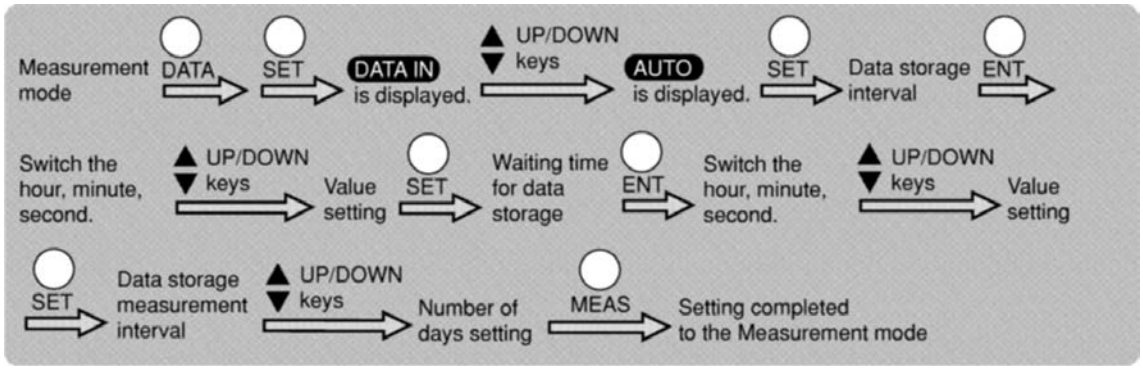
4.2 Automatic data storage

Measured values are stored automatically at constant time intervals. Before using the automatic storage, the following condition settings are required:

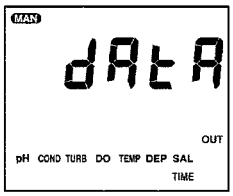
- Setting of data storage interval (4.2.1, step 4)
- Setting of waiting time for data storage (4.2.1, step 6)
- Setting of the data storage measurement period (4.2.1, step 8)



4.2.1 Data memory conditions settings



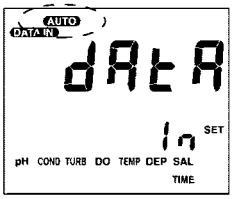
1. Press the **DATA** key in the Measurement mode.



2. Press the **SET** key.

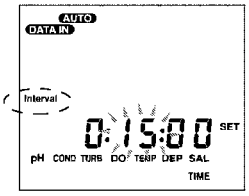
DATA IN is displayed.

3. Press the **UP/DOWN** (▲ ▼) keys to display **AUTO**.



4. Press the **SET** key to display the screen for setting the data storage interval Ⓐ.
"**Interval** " is displayed.

5. Press the **ENT** key to switch the among "hour", "minute" and "second" and set the value using the **UP/DOWN** (▲ ▼) keys.
(Data storage intervals can be set to 2 seconds to 24 hours.)
The current setting location will blink.

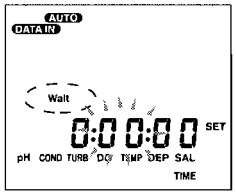


6. Press the **SET** key to display the screen for setting the waiting time for data storage Ⓑ.
"**Wait** " is displayed.

7. Press the **ENT** key to switch among "hour", "minute" and "second" and set the value using the **UP/DOWN** (▲ ▼) keys.
(The waiting time for data storage can be set to 2 seconds to 24 hours.)
The current setting location will blink.

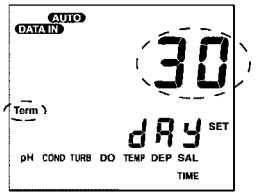
Important

- If wait time is set to "0", note that data is not stored in a memory the first time.



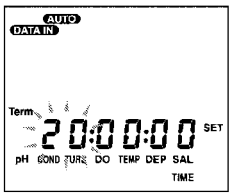
8. Press the **SET** key to display the screen for setting the data storage measurement period Ⓒ (number of days).
"**Term** " is displayed.

9. Use the **UP/DOWN** (▲ ▼) keys to set the value (number of days).



Setting of less than 24 hours

First set the number of days to 00 then press ENT key to select the "hour/minute/second" setting. Use the UP/DOWN (▲ ▼) keys to set the hour, the minute and second. During setting, the number to be set blinks.

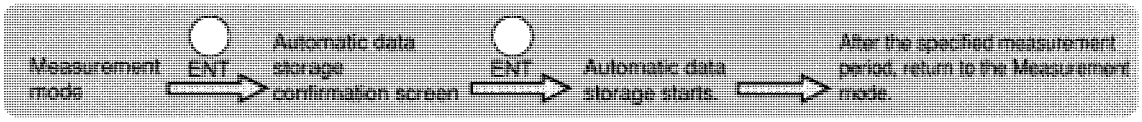


Note

- Press the SET key to return to step 4.

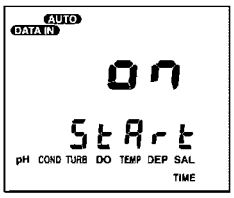
10. When the **MEAS** key is pressed, setting will be completed and the instrument will return to the Measurement mode.

4.2.2 Start of automatic data storage



1. Make sure that **AUTO** is displayed on the Measurement mode.

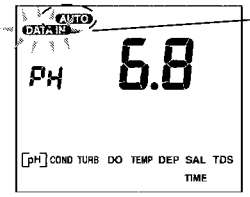
2. Press the **ENT** key. A confirmation screen will be displayed asking if you wish to start automatic data storage.



Note

- If you do not wish to proceed with automatic data storage, press the CAL key to return to the Masurement mode.

3. Press the **ENT** key to start automatic data storage.



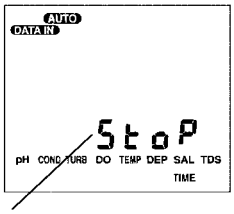
While **DATA IN** is blinking, the automatic data storage is being executed.

Note

- During the automatic data storage, measurement items can be switched by pressing the MEAS key.

Important

- During the automatic data storage, the ENT, SET, and DATA keys do not function and therefore calibration, setting change and stored data display cannot be performed.
- To stop automatic data storage, press the CAL key.



Confirmation display for canceling automatic data storage appears.
To stop the automatic data storage ..... Press the ENT key.
To return to the screen for the automatic data storage ... Press the DATA key.

4. After the specified measurement period, DATA IN disappears and the instrument returns to the normal Measurement mode.

Note

- When the instrument is turned on, AUTO lights up and DATA IN blink if automatic data storage is being performed with the sensor probe.

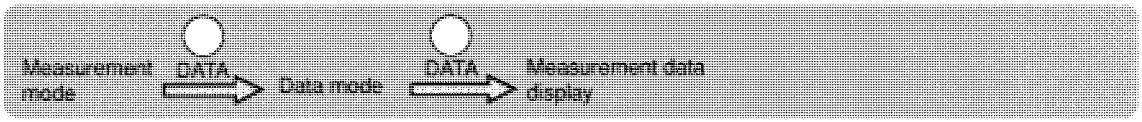
Notes for automatic data storage

- For long-term data storage, replace the sensor probe battery with a new one.
- You can remove the connector from the main unit. It can still be used for up to 60 hours at room temperature with the battery in the sensor probe (alkaline battery). Life is reduced by approximately one half when manganese batteries are used.
- If the sensor probe is connected to the instrument for monitoring, the instrument battery is first consumed to protect the memory of the sensor.
- When 2880 sets of data have been stored in the memory, ERR 9 appears and no more data can be stored. The automatic data storage is automatically ended and the instrument returns to the normal Measurement mode.

4.3 Calling up data from the memory

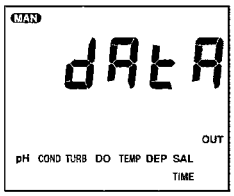
4.3.1 Calling up measurement data

Reading out data that has been stored manually or automatically.



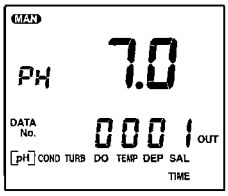
1. Press the **DATA** key in the Measurement mode.

The instrument goes to the DATA mode.



2. Press the **DATA** key.

The measurement data is displayed.
Data you want to call can be displayed by selecting a measurement item and data No.



DATA key ..... Selects switching of measurement item or memory data No.

When switching measurement items: Measurement item blinks.
When switching data No. : Data No. blinks.

UP/DOWN (▲▼) keys .... Switch measurement item or No. which has been selected with the DATA key.

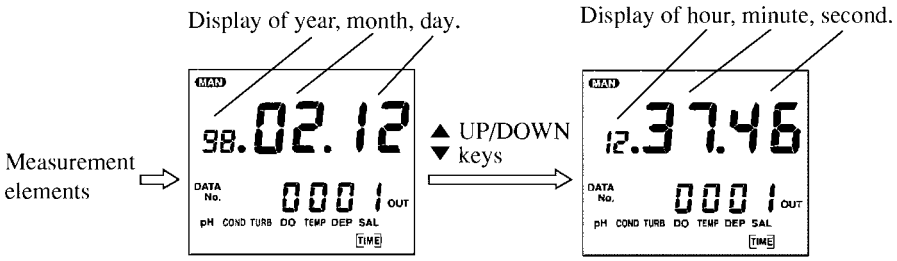
Note

- If you push the CAL key, only the data numbers will be displayed, allowing rapid changing of the numbers. Push the UP/DOWN (▲▼)keys to find the number, then press the SET key to display the data.

3. Press the **DATA** key.

TIME data

Use the UP/DOWN (▲▼) keys to switch between "Yer, Month, Day" and "Hour, Minute, Second".

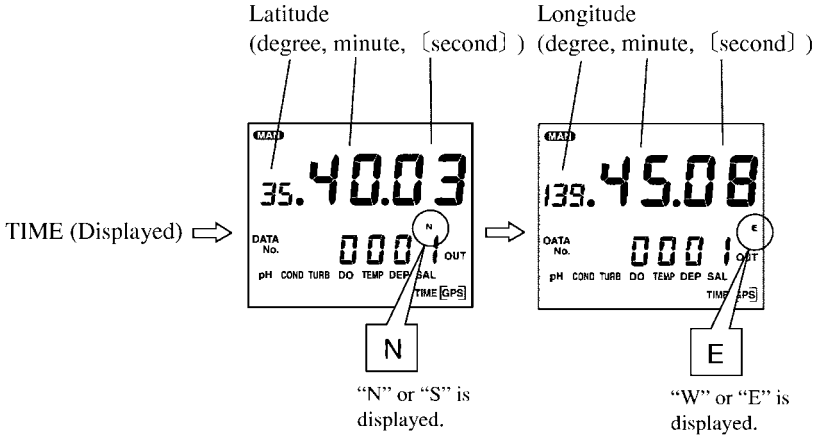


Note

- The time in the automatic memory can be out by about 2 seconds.

G.P.S. data (only when G.P.S. data is present)

Use the UP/DOWN (▲▼) keys to switch between "Latitude" and "Longitude".



Latitude N → The North latitude S → The South latitude
Longitude E → The East longitude W → The West longitude

ENT key ..... Prints all measurement data for the displayed memory data item.
(when the printer is connected to the instrument)

Useful uses of keys in automatic storage

SET + UP (▲) key ..... Displays the first part of the next data automatically stored.
SET + DOWN (▼) key ..... Displays the first part of the previous data automatically stored.
If there is manual data, then the previous or next manual data is shown.

Display for automatic storage

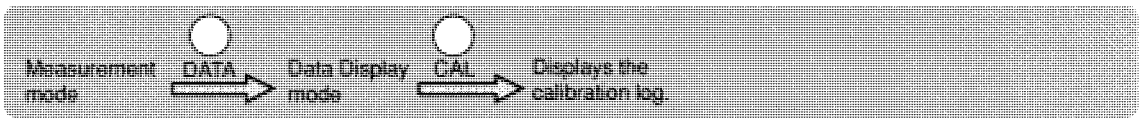
For the first and last data in one session of automatic storage the following identification marks are displayed in front of the values representing the data Nos.:
[: displayed for the first data in automatic storage.
] : displayed for the last data in automatic storage.

Note

- When the MEAS key is pressed, data calling is stopped and the instrument returns to the Measurement mode.
- Data is called from the sensor probe so to get one piece of data takes about one second.

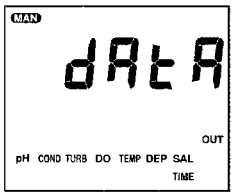
4.3.2 Calling up the calibration log

A calibration log is a record containing the "year, month, day" and "hour and minute" of the last calibration of individual measurement items and their calibration method. The instrument automatically stores the calibration log.



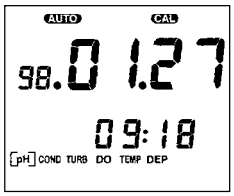
1. Press the **DATA** key in the Measurement mode.

The instrument goes to the DATA Display mode.



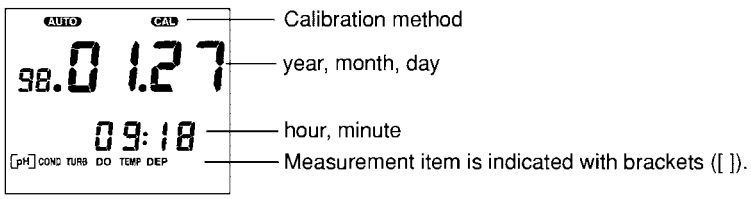
2. Press the **CAL** key.

The calibration log is displayed.



UP/DOWN (▲▼) keys: Switch the measurement item.
ENT key: Prints the entire calibration log. (when the printer is connected to the instrument)

Calibration log.



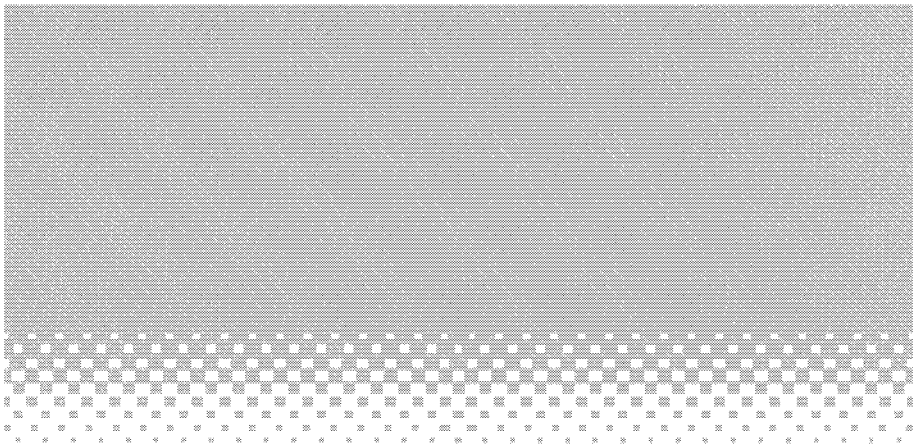
Calibration method

AUTO CAL	: AUTO calibration
MAN ZERO CAL	: Manual zero calibration
MAN SPAN CAL	: Manual span calibration
MAN ZERO SPAN CAL	: Manual zero calibration and span calibration

Note

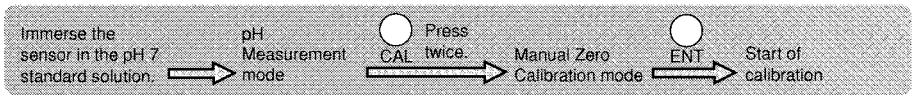
- Press the MEAS key to abort the data calling and return to the Measurement mode.

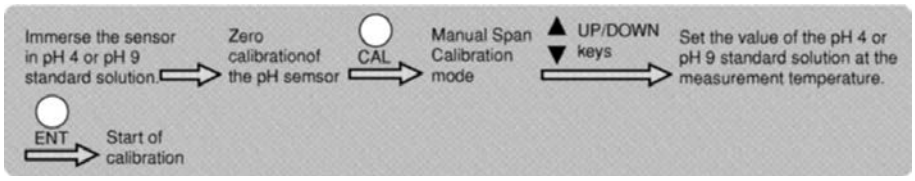
MEMO

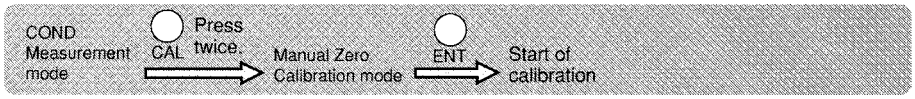


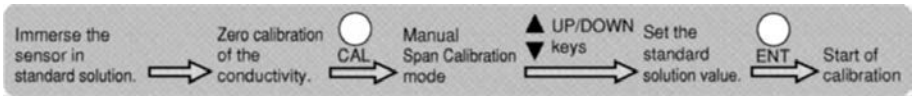
5. Techniques for more accurate measurement

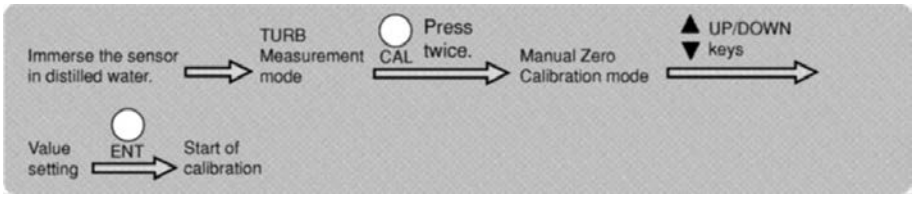
In normal operation, calibration using the AUTO Calibration mode described earlier in the basic operation section provides sufficient accuracy. However, for more accurate measurement, manual calibration is effective. When measurement with high-accuracy extended display is needed, be sure to perform manual calibration.
Attention: The extended display mode is entered automatically when manual calibration is selected.

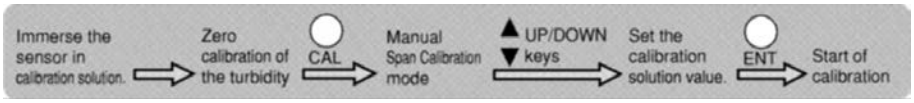


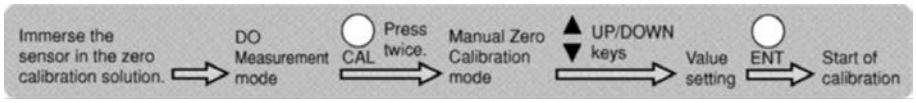


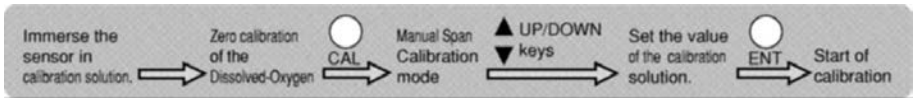


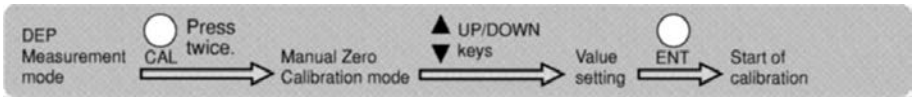


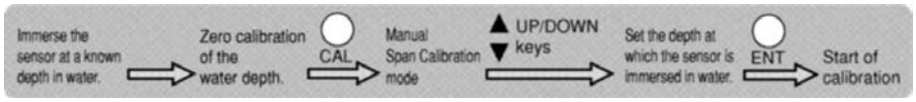


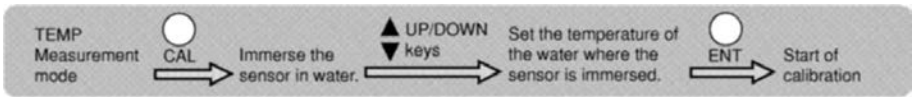






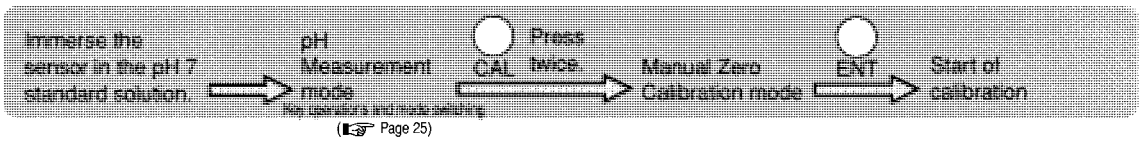






5.1 Manual pH calibration

5.1.1 Zero calibration

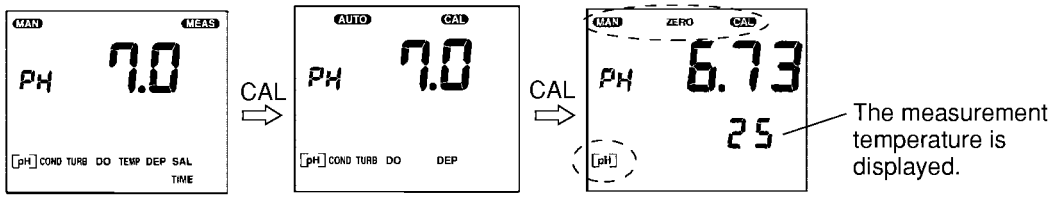


(☞ Page 25)

1. Wash the sensor two or three times using distilled water, then pour some pH 7 standard solution into the calibration beaker, and immerse the sensor in it.

2. Press the **CAL** key twice in the pH Measurement mode.

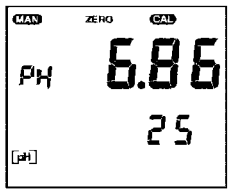
When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.



Manual Zero Calibration mode

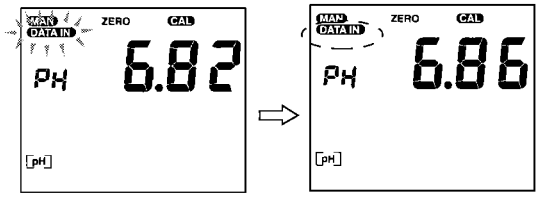
3. Use the **UP/DOWN** (▲ ▼) keys to input the value for the pH 7 standard solution at the measurement temperature.

(☞ *8. Reference data*, page 96.)



4. Press the **ENT** key.

The manual zero calibration starts.



End of calibration

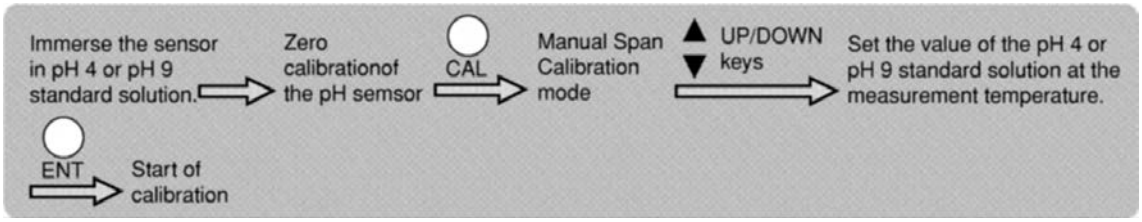
The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

To stop calibrating the sensor .... Press the CAL key.

To establish the calibration ..... Press the ENT key.

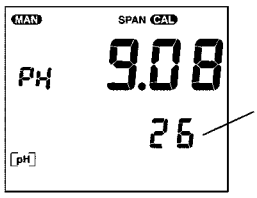
5.1.2 Span calibration



1. Wash the sensor two or three times using distilled water, then pour some pH 4 or pH 9 standard solution into the calibration beaker, and immerse the sensor in it.

2. After the zero calibration of the pH sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
MAN, **SPAN** and **CAL** light up.

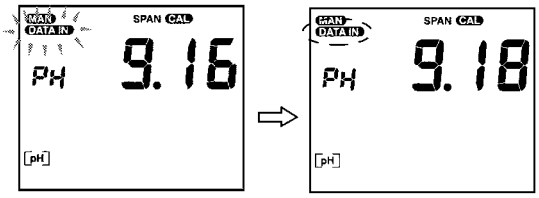
3. Use the **UP/DOWN** (▲ ▼) keys to set the value for the pH 4 or pH 9 standard solution at the measurement temperature.



The measurement temperature is displayed.

4. Press the **ENT** key.

The manual span calibration starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

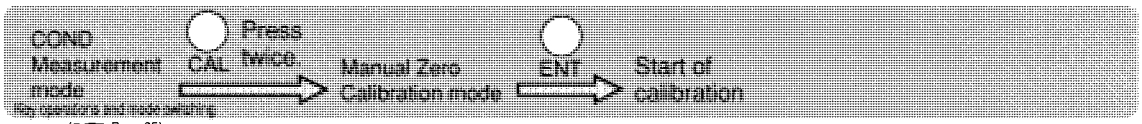
Note

- When the SET and CAL keys are pressed during the manual pH calibration mode, the calibration data for the pH sensor can be deleted.

5.2 Manual conductivity (COND) calibration

The U-20XD series models can measure conductivity (COND) in the range from 0.90 to 9.99 S/m. Depending on the concentration of the sample, these models automatically select the most suitable measuring range from three ranges: 0.0 to 99.9 mS/m, 0.090 to 0.999 S/m, and 0.90 to 9.99 S/m. The zero point is common to the three measuring ranges.

5.2.1 Zero calibration

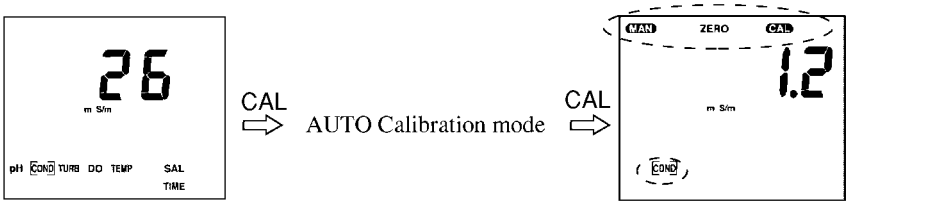


(☞ Page 25)

1. Wash the conductivity (COND) sensor two or three times using distilled water. Completely remove the water on the sensor and calibrate the instrument in the atmosphere.

2. Press the **CAL** key twice in the Conductivity (COND) Measurement mode.

When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.

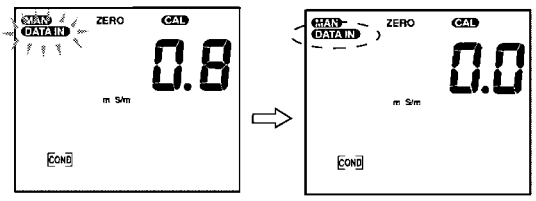


Manual Zero Calibration mode

3. Use the **UP/DOWN** (▲ ▼) keys to set the value to 0.0.

4. Press the **ENT** key.

The manual zero calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

To stop calibrating the sensor .... Press the CAL key.

To establish the calibration ..... Press the ENT key.

5.2.2 Span calibration

Preparation of calibration solution (Potassium chloride (KCl) standard solution)

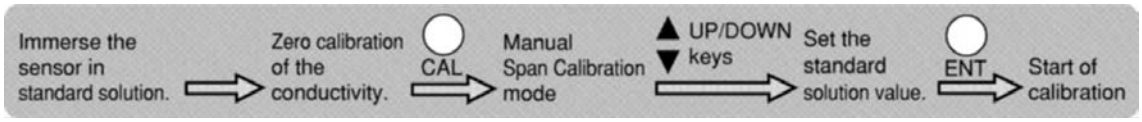
Dry Potassium chloride (KCl) powder (high-grade commercially available) at 105 °C for two hours, and leave it to cool in a desiccator.
Consult the following table and measure a portion of potassium chloride (KC1), then prepare standard potassium chloride (KC1) solution following the procedure below.

Potassium chloride (KCL) standard solution	Conductivity (COND) value	Potassium chloride (KCl) mass (g) at solution temperature of 25 °C	Calibration range
0.005 mol/L	71.8 mS/m	0.373	0.0 to 99.9 mS/m
0.050 mol/L	0.667 S/m	3.73	0.090 to 0.999 S/m
0.500 mol/L	5.87 S/m	37.2	0.90 to 9.99 S/m

1. Dissolve the weighed Potassium Chloride (KCl) in distilled water.
2. Put the dissolved Potassium Chloride (KCl) into a 1 L measuring flask, and fill to the 1 L mark with distilled water.

Calibration procedure

Perform the span calibration using the three types of standard solution as follows.

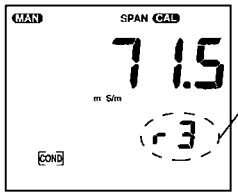


Important

- Set the temperature of the span standard solution to 25 ± 5 °C.
- The sensor should be calibrated in the three standard solutions in the order of increasing concentration.

1. Wash the sensor two or three times using distilled water, then pour some standard solution into the calibration beaker, and immerse the sensor in it.
2. After the zero calibration of the conductivity (COND) sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
MAN, **SPAN** and **CAL** light up.

3. Use the **UP/DOWN** (▲ ▼) keys to set the standard solution value.



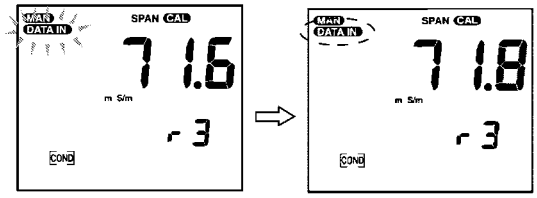
The calibration range is displayed.

Note

- The sensor automatically identifies the calibration solution and the relevant calibration range is displayed.
  - r 1 : 0.90 to 9.99 S/m
  - r 2 : 0.090 to 0.999 S/m
  - r 3 : 0.0 to 99.9 mS/m

4. Press the **ENT** key.

The manual span calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

To stop calibrating the sensor .... Press the CAL key.

To establish the calibration ..... Press the ENT key.

5. Press the **CAL** key and use each standard solution and perform steps 1 to 4 above for calibration.

6. Press the **MEAS** key to return to the Measurement mode.

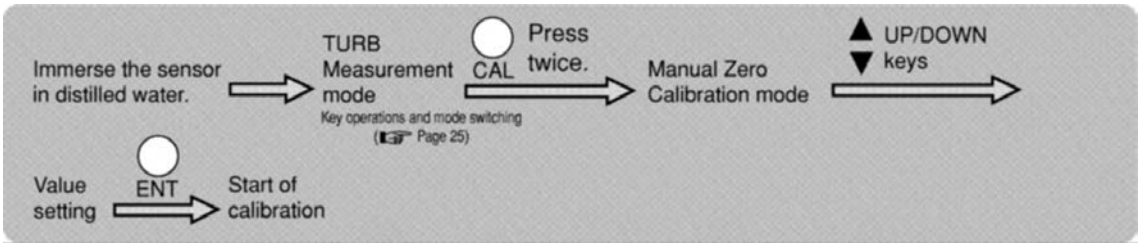
Note

- When the SET and CAL keys are pressed during the manual Conductivity (COND) Calibration mode, the calibration data for the conductivity (COND) sensor can be deleted.
- Perform the calibration again after deleting the present calibration data when calibration error occurs and the calibration cannot be performed.
- Perform the calibration again after deleting the present calibration data when the value cannot be read off because of unsettled digit of the measurement value.

5.3 Manual turbidity (TURB) calibration

5.3.1 Zero calibration

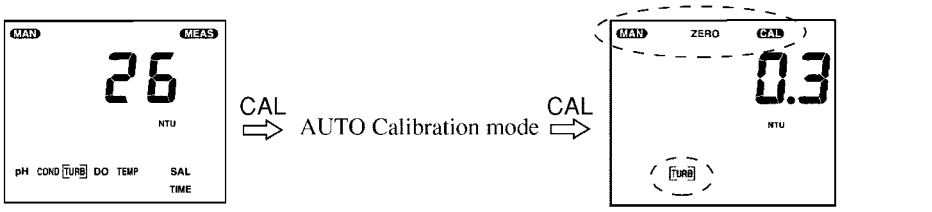
In zero calibration, distilled water is used as a calibration solution. If you cannot obtain distilled water, you may use ion exchange water, which can be considered to have a turbidity of zero.
When the turbidity (TURB) sensor is calibrated, it is particularly important that the probe is completely contamination-free. Do not use a contaminated probe. Otherwise unreliable calibration will result.



1. Wash the sensor two or three times using distilled water, then place some distilled water into the calibration beaker, and immerse the sensor in it.

2. Press the **CAL** key twice in the Turbidity (TURB) Measurement mode.

When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.

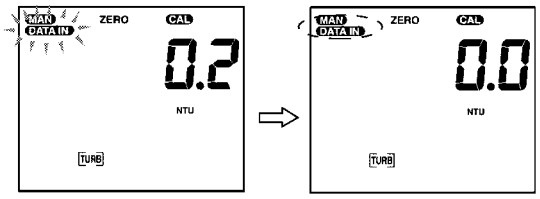


Manual Zero Calibration mode

3. Use the **UP/DOWN** (▲ ▼) keys to set the value to 0.0.

4. Press the **ENT** key.

The manual zero calibration is started.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

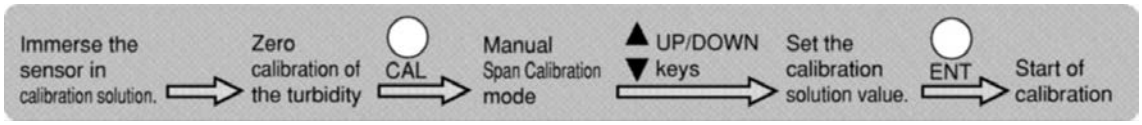
With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5.3.2 Span calibration

Preparation of calibration solution

Weigh out 5.0 g of hydrazine sulfate, and dissolve it in 400 mL of distilled water. Next dissolve 50 g of hexamethylene tetramine in 400 mL of distilled water, and mix the two solutions together. Finally add distilled water until the total solution volume is 1000 mL, and mix well. Store this solution at a temperature of 25 ± 3 °C for 48 hours. The turbidity value (TURB) of this solution is equivalent to 4000 NTU.
Use the solution as span calibration solution for turbidity (TURB) of 800 NTU by diluting this solution by a factor of 5 (use a pipette to measure 50 mL of the 4000 NTU solution and pour it into a 250 mL measuring flask, and add 200 mL of distilled water).

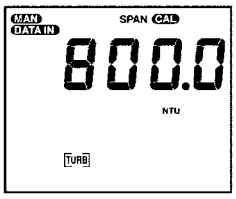
Calibration procedure



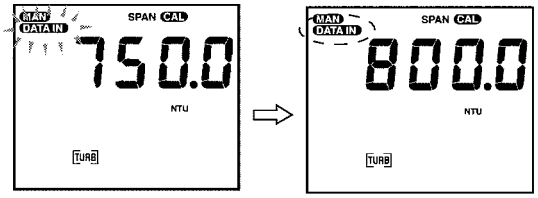
1. Wash the sensor two or three times using distilled water, then pour standard solution into a calibration beaker, and immerse the sensor in it.

2. After the zero calibration of the turbidity (TURB) sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
MAN, **SPAN** and **CAL** light up.

3. Use the **UP/DOWN** (▲ ▼) keys to set the value to 800.0.



4. Press the **ENT** key.
The manual span calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Important

- When it is known beforehand that the solution for measurement has a low turbidity (0 to 100 NTU), calibrate the sensor in the span calibration solution of 80 NTU. To prepare an 80 NTU calibration solution, dilute the 4,000 NTU calibration solution with distilled water by a factor of 50.

Note

- When the SET and CAL keys are pressed during the manual Turbidity (TURB) Calibration mode, the calibration data for the turbidity (TURB) sensor can be deleted.

5.4 Manual Dissolved-Oxygen (DO) calibration

It is necessary to prepare a new calibration solution each time directly before calibration of the Dissolved-Oxygen (DO) sensor.

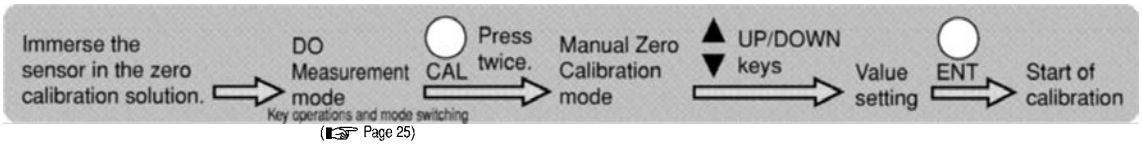
5.4.1 Zero calibration

Use ion exchange water or tap water with sodium sulfite dissolved in it.

Preparation of calibration solution

Add approximately 50 g of sodium sulfite to 1,000 mL of water (either ion exchange water or tap water) and stir the mixture to dissolve the sodium sulfite in it.
The calibration beaker (included) cannot be used to manually calibrate the DO sensor. Use a container that can immerse the DO sensor.

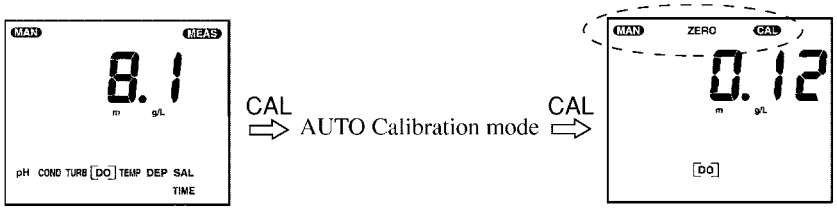
Calibration procedure



1. Wash the sensors 2 to 3 times with pure water and immerse the DO sensor completely in zero calibrated liquid.

2. Press the **CAL** key twice in the Dissolved-Oxygen (DO) Measurement mode.

When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.

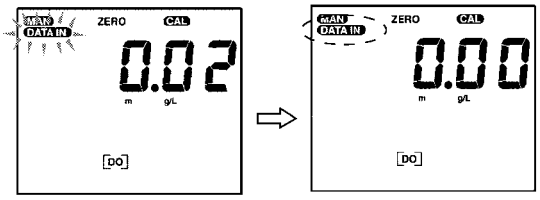


Manual Zero Caliburation mode

3. After the display has stabilized, use the **UP/DOWN** (▲ ▼) keys to set the value to 0.0.

4. Press the **ENT** key.

The manual zero calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

Important

- After calibration, use tap water to clean the sensor.

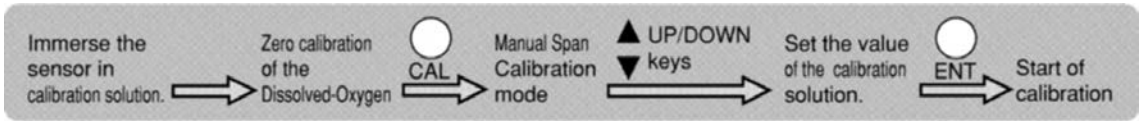
5.4.2 Span calibration

Use ion exchange water or tap water with saturated dissolved oxygen as the span calibration liquid.

Preparation of standard solution for span calibration

Pour 1 to 2 liters of water into a container (either ion exchange water or tap water).
Using a pneumatic pump, feed air into the water and froth up the solution until oxygen is saturated.
The calibration beaker (included) cannot be used to manually calibrate the DO sensor.
Use a container that can immerse the DO sensor.

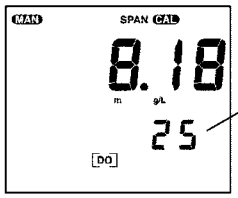
Calibration procedure



1. Wash the sensors 2 to 3 times with pure water and immerse the DO sensor completely in span calibrated liquid.

2. After the zero calibration of the Dissolved-Oxygen (DO) sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
MAN, **SPAN** and **CAL** light up.

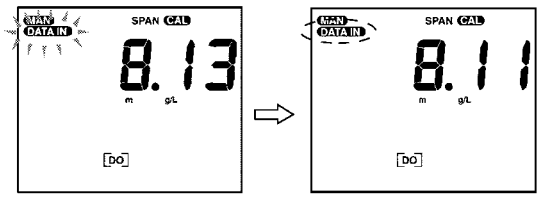
3. After the display has stabilized, use the **UP/DOWN** (▲ ▼) keys to set the amount of saturated dissolved oxygen in water at the temperature.



The temperature setting is displayed.
Refer to the table given on page 56 and set a value equivalent to the amount of saturated dissolved oxygen at the temperature.

4. Press the **ENT** key.

The manual span calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Note

- When the SET and CAL keys are pressed during the manual Dissolved-Oxygen (DO) calibration mode, the calibration data for the dissolved-oxygen (DO) sensor can be deleted.

Amounts of saturated dissolved oxygen in water at various temperatures (salinity=0.0%)

JIS K0101

Temp. (°C)	DO (mg/L)	Temp. (°C)	DO (mg/L)	Temp. (°C)	DO (mg/L)	Temp. (°C)	DO (mg/L)
0	14.16						
1	13.77	11	10.67	21	8.68	31	7.42
2	13.40	12	10.43	22	8.53	32	7.32
3	13.04	13	10.20	23	8.39	33	7.22
4	12.70	14	9.97	24	8.25	34	7.13
5	12.37	15	9.76	25	8.11	35	7.04
6	12.06	16	9.56	26	7.99	36	6.94
7	11.75	17	9.37	27	7.87	37	6.86
8	11.47	18	9.18	28	7.75	38	6.76
9	11.19	19	9.01	29	7.64	39	6.68
10	10.92	20	8.84	30	7.53	40	6.59

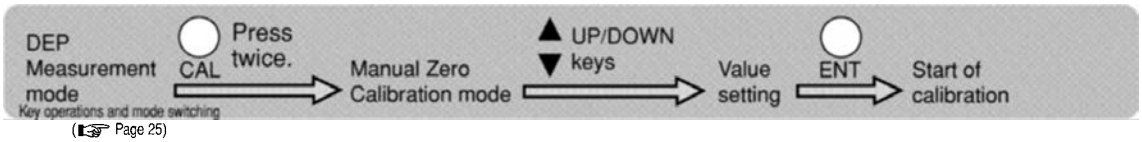
ISO5814

Temp. (°C)	DO (mg/L)	Temp. (°C)	DO (mg/L)	Temp. (°C)	DO (mg/L)
0	14.62				
1	14.22	11	11.03	21	8.91
2	13.83	12	10.78	22	8.74
3	13.46	13	10.54	23	8.58
4	13.11	14	10.31	24	8.42
5	12.77	15	10.08	25	8.26
6	12.45	16	9.87	26	8.11
7	12.45	17	9.66	27	7.97
8	11.84	18	9.47	28	7.83
9	11.56	19	9.28	29	7.69
10	11.29	20	9.09	30	7.56

AUTO calibration is based on the JIS tables. When you need the measured data based on ISO, calibration should be done according to the procedure of span calibration.

5.5 Water depth (DEP) calibration

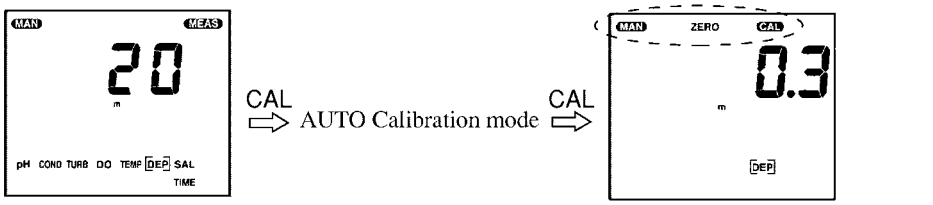
5.5.1 Zero calibration



1. Immerse the sensor in the sample water for approximately 30 minutes so that sensor probe and sample temperatures become the same.

2. Press the **CAL** key twice in the Water Depth (DEP) Measurement mode.

When the instrument enters the Manual Zero Calibration mode, **MAN**, **ZERO** and **CAL** light up.



Manual Zero Calibration mode

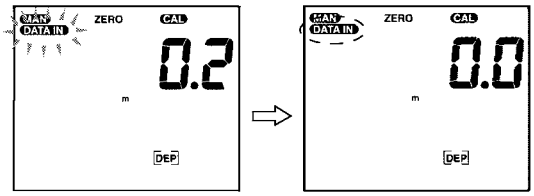
Important

- Sensor probe should be immersed to the depth where the battery cover comes level with the surface. And the level is uses as 0 m in depth.

3. Use the **UP/DOWN** (▲ ▼) keys to set the value to 0.0.

4. Press the **ENT** key.

The manual zero calibration is starts.



End of calibration

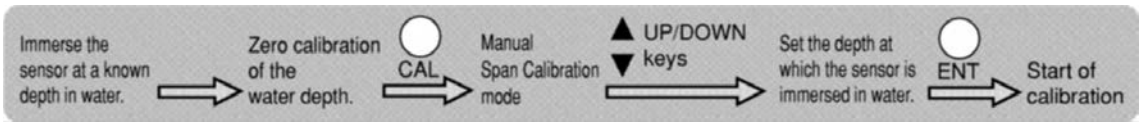
The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

Important

- Since the water depth (DEP) sensor depends greatly on temperature, calibrate the sensor at the same temperature as the sample for more accurate measurement.
- Use the AUTO Calibration mode because calibration error becomes large when using in a place with flow velocity or where it is shallow.

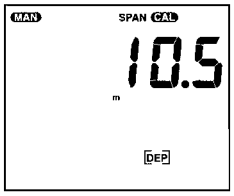
5.5.2 Span calibration



1. Immerse the sensor at a known depth in water. (Set the depth of the lid for memory backup battery as the depth setting.)

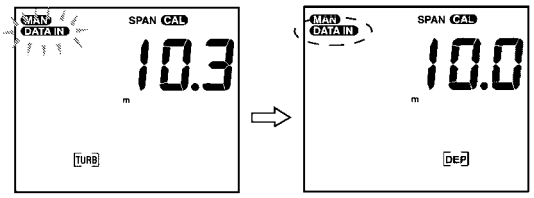
2. After the zero calibration of the water depth (DEP) sensor, press the **CAL** key to make sure that the instrument is in the Manual Span Calibration mode.
MAN, **SPAN** and **CAL** light up.

3. Use the **UP/DOWN** (▲ ▼) keys to set the depth at which the sensor is immersed in water.



4. Press the **ENT** key.

The manual span calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

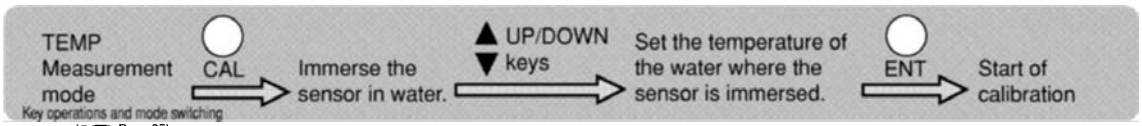
With DATA IN is blinking
To stop calibrating the sensor .... Press the CAL key.
To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Note

- When the SET and CAL keys are pressed during the manual Water depth (DEP) Calibration mode, the calibration data for the water depth (DEP) sensor can be deleted.

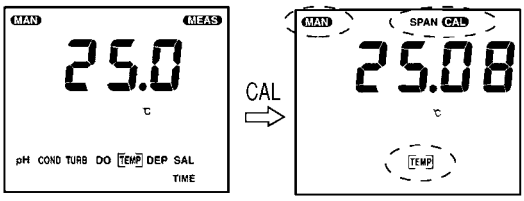
5.6 Temperature (TEMP) calibration



Key operations and mode switching
(☞ Page 25)

1. Press the **CAL** key in the Temperature (TEMP) Measurement mode.

Select the manual calibration mode.

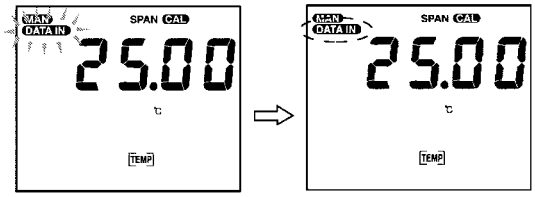


2. Immerse the sensor in water at a known temperature.

3. Use the **UP/DOWN** (▲ ▼) keys to set the temperature of the water where the sensor is immersed as a calibration value.

4. Press the **ENT** key.

The manual calibration is starts.



End of calibration

The measured value is displayed during calibration, and **DATA IN** blinks until the indicated value stabilizes. When the indicated value has stabilized, **DATA IN** lights up and the calibration finishes.

With DATA IN is blinking

To stop calibrating the sensor .... Press the CAL key.

To establish the calibration ..... Press the ENT key.

5. Press the **MEAS** key to return to the Measurement mode.

Note

- When the SET and CAL keys are pressed during the manual Temperature (TEMP) calibration mode, the calibration data for the temperature (TEMP) sensor can be deleted.

5.7 Operation check using ORP standard solution

Note

- Standard solution is not used only for calibration of the meter, but to confirm whether or not the condition of electrodes is good.

1. Add 250 mL pure (ion exchange) water to one packet of any of the below listed standard solutions and mix well.
   When mixing, the excess quinhydrone (a black powder) will float to the surface of the solution.
2. Immerse a washed and dried ORP electrode in the ORP standard solution and measure the mV value.
3. If the electrode and the meter, itself, are working correctly, numerical values within 15 mV or less of those listed in Table 1 should be obtained.
4. If measurements that fall within 15 mV of the values listed above are not obtained using this method, measure the solution again after replacing the reference electrode internal solution and removing the dirt from the surface of the metal electrode by moistening a cotton swab with alcohol or a neutral cleaning agent and lightly rubbing the electrode or by soaking the electrode in diluted nitric acid (1:1 nitric acid).
5. If measurements within 15 mV of the values listed above are still not obtained after re-measuring, the reference electrode or the meter may be faulty. Either replace the electrode or have the meter inspected.

Important

- If the prepared ORP standard solution is allowed to stand in open air for one hour or more, it may undergo transformation. For this reasons ORP standard solution that has finished being prepared cannot be stored.
- When measuring a solution that has low concentrations of oxidants and reductants after conducting an operational check using a standard substance, the measured values may not stabilize or the results of measurement might not be repeatable.
  If this is the case, use the meter after immersing the electrodes in the solution again and mixing it thoroughly.

Precautions when measuring actual samples

- Note that when measuring the ORP of solution that has extremely low concentrations of oxidants and reductants, such as tap water, well water, or water treated with purifying equipment, there may be less responsiveness, repeatability, and stability, in general.
- When alkaline water is allowed to stand, its ORP undergoes big changes. Always measure alkaline ion water promptly.

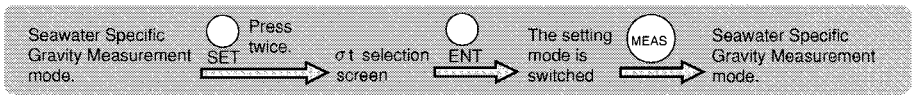
ORP standard solution

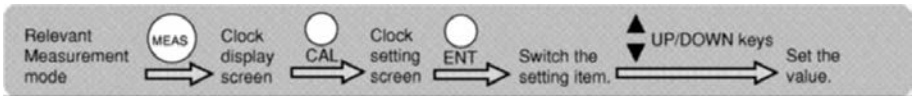
There are two kinds of standards substances. Under normal circumstances, it is sufficient to use only the one type of substance that is closest to the measured value.

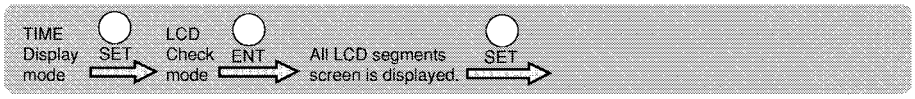
Indicated value of ORP standard solution at various temperatures

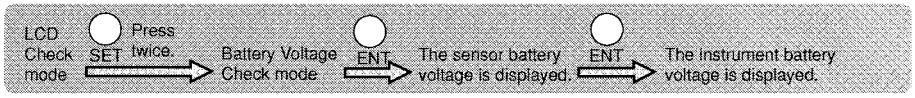
Standard solution ℃	160-22 Phthalic-acid chloride + quinhydrone	160-51 Neutral phosphate + quinhydrone
5	+274.2	+111.9
10	+270.9	+106.9
15	+266.8	+101.0
20	+262.5	+95.0
25	+257.6	+89.0
30	+253.5	+82.7
35	+248.6	+76.2
40	+243.6	+69.0

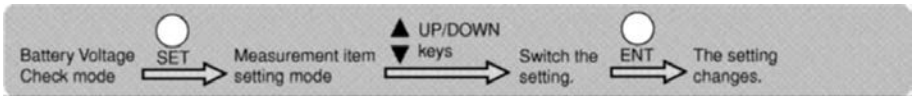
6. Using the various functions

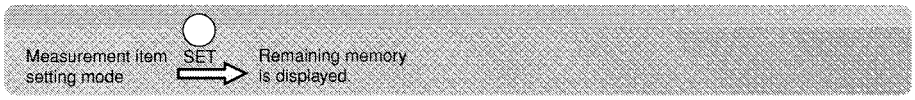


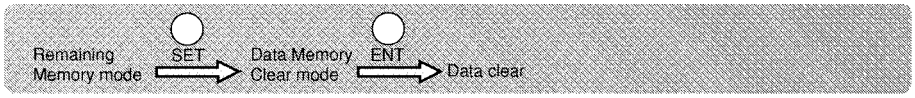


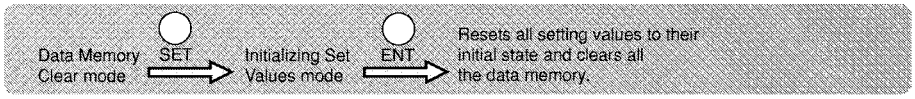


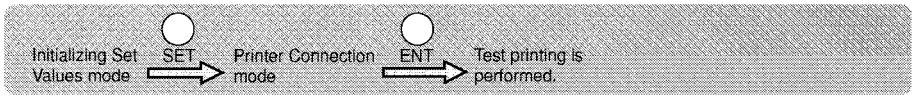






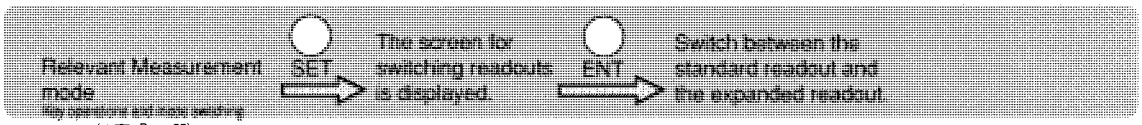






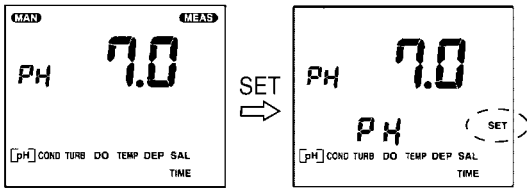
6.1 Switching to Expanded readout (High-accuracy display)

With the exception of oxidation-reduction potential (ORP), it is possible to switch between the Standard readout and the Expanded readout for the measurement value.



1. Press the **SET** key in the relevant Measurement mode.

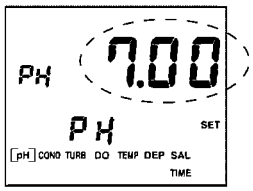
The screen for switching readouts is displayed.



Standard readout

2. Press the **ENT** key.

The screen can be switched between the standard readout and the expanded readout (High-accuracy display).



Expanded readout (High-accuracy display)

Note

- Switch readouts for each measurement items.
- Use the manual 2-point calibration (zero and span) when high accuracy is required for expanded readout (High-accuracy display).
- The expanded readout mode is automatically activated when the manual 2-point calibration mode is chosen.

3. Press the **MEAS** key to return to the Measurement mode.

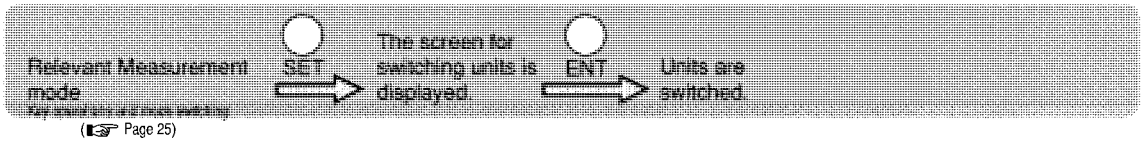
6.2 Switching measurement units

It is possible to switch between measurement units.

The units which can be switched are as follows:

pH ..... pH or mV
Conductivity (COND) ..... S/m or mS/cm
Water depth (DEP) ..... m or ft
Turbidity (TURB) ..... NTU or mg/L
Dissolved Oxygen (DO) ..... mg/L or % (Oxygen saturation ratio)

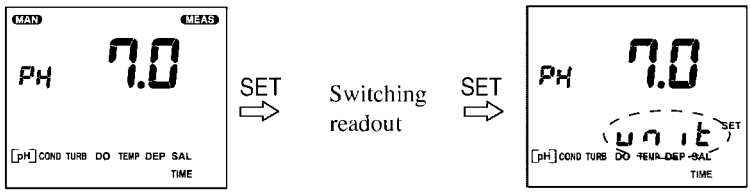
In the case of pH, TURB, DO



(☞ Page 25)

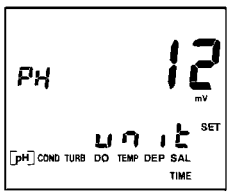
1. Press the **SET** key twice in the relevant Measurement mode.

Confirm that unit is displayed on the screen for switching units.



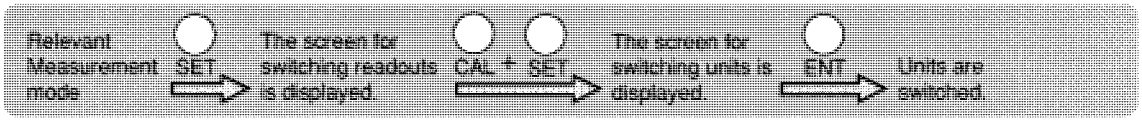
2. Press the **ENT** key.

Units are switched.



3. Press the **MEAS** key to return to the Measurement mode.

In the case of COND and DEP



1. Press the **SET** key in the Relevant Measurement mode.

The screen for switching readout is displayed.

2. Press the **SET** key while holding down the **CAL** key.

Confirm that **unit** is displayed on the screen for switching units.

3. Press the **ENT** key.

Units are switched.

4. Press the **MEAS** key to return to the Measurement mode.

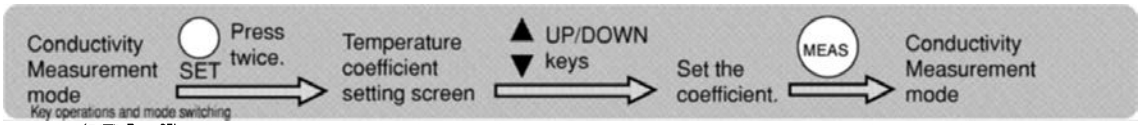
Measurement range

Measurement item		Measurement range		Measurement units
		Expanded	Standard	
pH		0.00 to 14.00	0.0 to 14.0	pH
		—	−1999 to 1999	mV in pH measurement
Conductivity (COND)	Range 1	0.90 to 9.99	0.9 to 9.9	S/m
		9.0 to 99.9	9 to 99	mS/cm
	Range 2	0.090 to 0.999	0.09 to 0.99	S/m
		0.90 to 9.99	0.9 to 9.9	mS/cm
	Range 3	0.0 to 99.9	0 to 99	mS/m
		0.000 to 0.999	0.00 to 0.99	mS/cm
Turbidity (TURB) *1		0.0 to 800.0	0 to 800	NTU (nephelometric turbidity units) or mg/L
Dissolved-oxygen (DO)		0.00 to 19.99	0.0 to 19.9	mg/L
		0.0 to 199.9	0 to 199	%
Temperature (TEMP)		0.00 to 55.00	0.0 to 55.0	°C
Water depth (DEP)		0.0 to 100.0	0 to 100	m
		0.0 to 330.0	0 to 330	ft
Salinity (SAL)		0.00 to 4.00	0.0 to 4.0	%
Total dissolved solids	Range 1	5.5 to 65.0	5 to 65	g/L
(TDS) *2	Range 2	0.55 to 6.50	0.5 to 6.5	g/L
	Range 3	0.000 to 0.650	0.00 to 0.65	g/L
Seawater specific gravity (σ_t)		0.0 to 50.0	0 to 50	–
Oxygen-reduction potential (ORP)		—	−1999 to 1999	mV

*1: Depending on the concentration range, the minimum turbidity is displayed as follows:
0 to 100 NTU ... 1 NTU for standard readout, 0.1 NTU for expanded readout.
100 to 800 NTU ... 10 NTU for standard readout, 1 NTU for expanded readout.
*2: The TDS range depends on the TDS factor settings. (Above ranges are given for a TDS coefficient of 0.65.)

6.3 Temperature conversion for conductivity (COND)

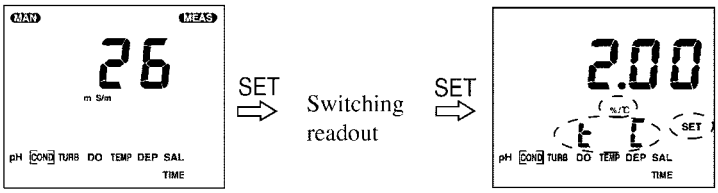
Sample conductivity (COND) varies with temperature, and this instrument uses a temperature conversion coefficient to automatically standardize the conductivity (COND) to the value at 25 °C. The initial setting value is 2 %/°C, which is the generally used value.



Key operations and mode switching (☞ Page 25)

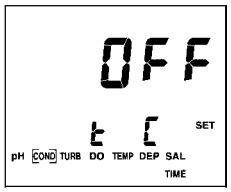
1. Press the **SET** key twice in the Conductivity (COND) Measurement mode.

The screen for setting temperature coefficients is displayed.



2. Use the **UP/DOWN** (▲ ▼) keys to set the coefficient.

The setting range is 0.00 to 3.00 %/°C.



With the ENT key, the temperature conversion is switched between ON and OFF.
The temperature conversion OFF mode is not a 25°C coefficient but a coefficient at the temperature of the sample.

3. Press the **MEAS** key.

The instrument returns to the Conductivity (COND) Measurement mode.

Note

- For temperature coefficients, refer to *Reference data*, page 98 to 99.

6.4 Dissolved-Oxygen (DO) environmental influence compensation

6.4.1 Salinity compensation

The indicated dissolved oxygen (DO) value can go over the actual value if salinity compensation isn't added because of the increase in salinity in the sample. To obtain a correct measured value for dissolved oxygen (DO) in the sample containing salinity, therefore, salinity compensation is needed. The following modes are available for calculation of salinity compensation.

AUTO..... Salinity compensation is performed automatically with salinity converted from a measured value for conductivity.

SEA ..... Compensation value appropriate for normal seawater is used.

(☞ Page 25)

1. Press the **SET** key 3 times in the Dissolved-Oxygen (DO) Measurement mode.

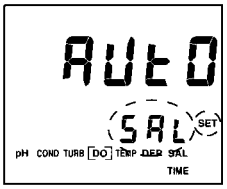
The salinity compensation mode currently set is displayed.

Important

- If you do not change the salinity compensation mode currently set, press the MEAS key to return to the Dissolved-Oxygen (DO) Measurement mode or press the SET key to select the Pressure Compensation mode.

2. Press the **ENT** key.

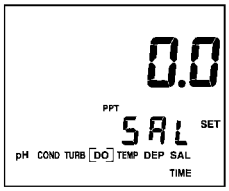
The following screens are displayed in sequence each time the ENT key is pressed: AUTO setting, value setting, SEA setting and AUTO setting.



3. From the screen on which the value is displayed, use the **UP/DOWN** (▲ ▼) keys to enter the setting value if the salinity is known.

For AUTO and SEA setting, this step need not be performed.

The setting range is 0.0 to 40.0 ppt (parts per thousand).

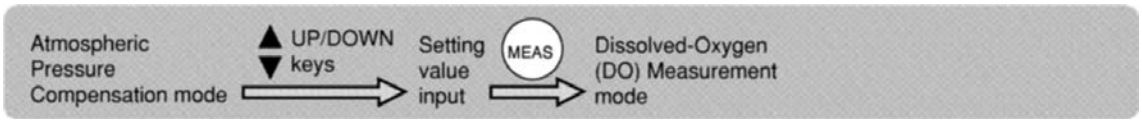


4. When the **SET** key is pressed, setting will be completed and the instrument will enter the Pressure Compensation mode.

5. Press the **MEAS** key to return to the Dissolved-Oxygen (DO) Measurement mode.

6.4.2 Atmospheric pressure compensation

Differences in the atmospheric pressure of the measurement location influence the Dissolved-Oxygen (DO) measurement. By setting (input) the actual atmospheric pressure of the measurement location into the instrument, it is possible to standardize the measured Dissolved-Oxygen (DO) value to a value at the standard atmospheric pressure (1013 hPa).



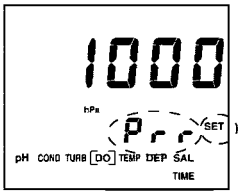
1. When the **SET** key is pressed on the salinity compensation screen, setting will be completed and the instrument will enter the Pressure Compensation mode.

Important

- If you do not change the Pressure Compensation mode currently set, press the MEAS key to enter the Dissolved-Oxygen (DO) Measurement mode.

2. Use the **UP/DOWN** (▲ ▼) keys to input a setting value.

The setting range is 100 to 1999 hPa.



3. When the **MEAS** key is pressed, setting will be completed and the instrument will enter the Dissolved-Oxygen (DO) Measurement mode.

Relation between height (m) and atmospheric pressure (hPa)

Height (m)	0	200	400	600	800	1000	1200	1400	1600	1800	2000	3000	3400
Pressure (hPa)	1013	990	966	943	921	899	877	856	835	815	795	701	666

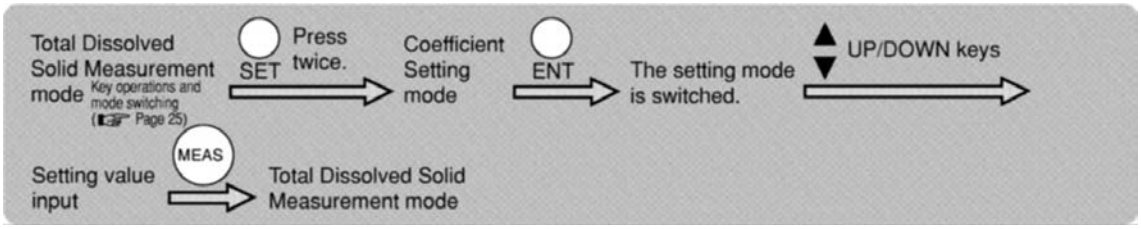
6.5 Setting a total dissolved solid (TDS) coefficient

The total dissolved solid amount (TDS) is a converted value obtained by multiplying the conductivity (COND) value by a known coefficient. Based on a conversion for KCl and $CaCO_3$ solutions, the coefficient initially set for the instrument depends on the conductivity (COND) value as shown below.

Conductivity (COND) (S/m)	Conversion coefficient
< 0.05	0.65
0.05 to 0.5	0.64
0.5 to 1	0.63
1 to 3	0.62
3 to 5	0.61
> 5	0.60

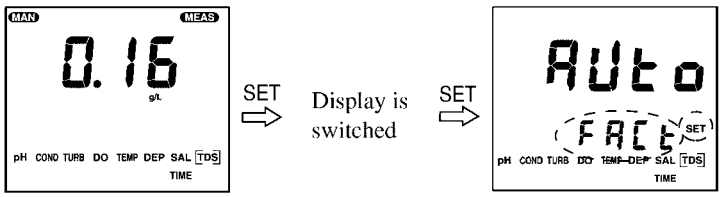
AUTO ..... Used to automatically calculate the total dissolved solid (TDS) amount with an initially set coefficient.

Setting value input ..... Used to determine the total dissolved solid (TDS) amount by setting any conversion coefficient irrespective of the conductivity (COND) value.



1. Press the **SET** key twice in the Total Dissolved Solid (TDS) Measurement mode.

The Coefficient Setting mode currently set is displayed.

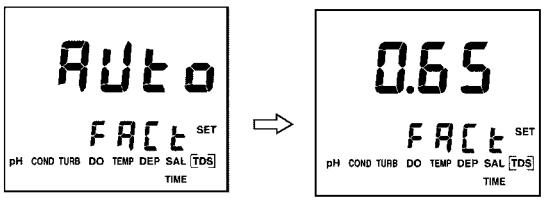


Important

- If you do not change the coefficient currently set, press the MEAS key to enter the Total Dissolved Solid (TDS) Measurement mode.

2. Press the **ENT** key.

The setting mode changes (AUTO/setting value input).



3. Use the **UP/DOWN** (▲ ▼) keys to input a setting value if required.

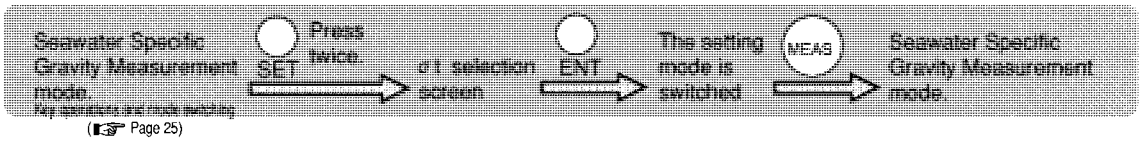
The setting range is 0.50 to 1.00.

4. When the **MEAS** key is pressed, setting will be completed and the instrument will enter the Total Dissolved Solid (TDS) Measurement mode.

6.6 Displaying seawater specific gravity (σ_0, σ_{15})

The specific gravity of seawater varies with temperature. By converting the measured value based on the value for a reference temperature, it is possible to compare sample measurement values at different temperatures.

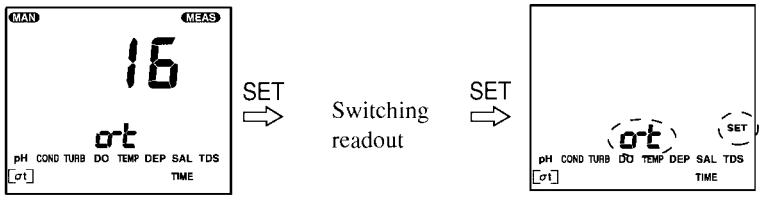
σ_t ..... Specific gravity of seawater at the measurement temperature.
σ_0 ..... Seawater specific gravity at 0 °C.
σ_{15} ..... Seawater specific gravity at 15 °C.



(☞ Page 25)

1. Press the **SET** key twice in the Seawater Specific Gravity (σ_t) Measurement mode.

Seawater specific gravity (σ_t) selection screen is displayed.

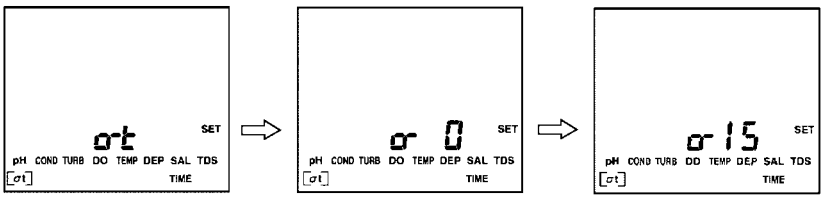


Important

- If you do not change the specific gravity currently set, press the MEAS key to enter the Seawater Specific gravity (σ_t) Measurement mode.

2. Press the **ENT** key.

The setting mode is switched.
($\sigma_0 \rightarrow \sigma_{15} \rightarrow \sigma_t \rightarrow \sigma_0 \ldots$)

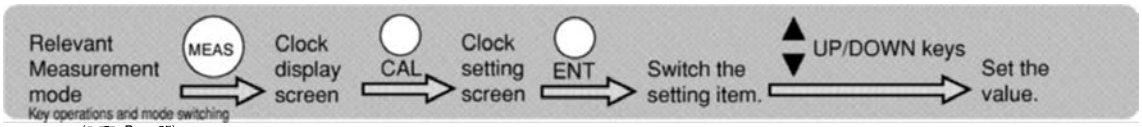


3. When the **MEAS** key is pressed, setting will be completed and the instrument will enter the Seawater Specific Gravity (σ_t) Measurement mode.

Note

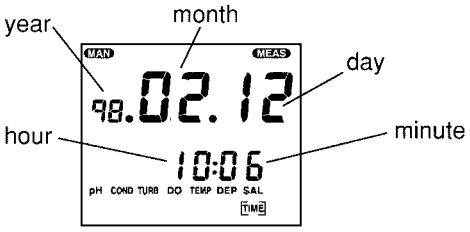
- See page 100 for more about seawater specific gravity.

6.7 Setting the clock



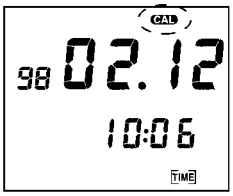
Key operations and mode switching
(☞ Page 25)

1. Use the **MEAS** key in the measurement mode to switch to the clock display screen.



2. Press the **CAL** key.

CAL light up and clock setting screen is displayed.



3. Press the **ENT** key to switch the measuring item.

(year → month → day → hour → minute → year ...). The setting item will blink.

4. Use the **UP/DOWN** (▲ ▼) keys to set the value.

5. Press **SET** key to confirm the setting.

Note

- When the MEAS key is pressed, the instrument will return to the clock display.

Important

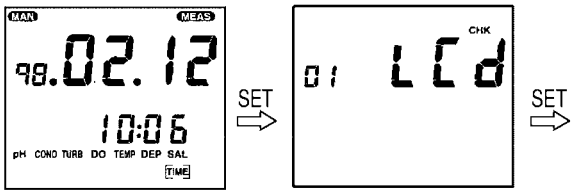
- When the MEAS key is pressed without pressing the SET key and the clock display is displayed again, settings are not changed.

6.8 Key lock setting

If you press the POWER key while pressing the UP (▲) key when the power is off, the instrument is then turned ON with the key locked and the key lock function works.
With the key locked, only the POWER and MEAS keys can be used and [LOCK] is displayed on the screen. To release this function, turn the instrument OFF first and then ON again.

6.9 Check mode

When the SET key is pressed in the measurement mode from the screen where "year, month, day and time" are displayed, the instrument performs self-diagnosis check.



Each time the SET key is pressed, the check mode item is switched sequentially.

Check mode items

1 :	LCD check	Checks if all LCD segments will be displayed. (☞ Page 74)
2 :	Battery voltage check	Performs a simple battery voltage check for the instrument and sensors. (☞ Page 75)
3 :	Measurement item setting	Can set the measurement item to be stored. (☞ Page 76)
4 :	Remaining memory	Displays the number of data that can be stored now. (☞ Page 77)
5 :	Data memory clear	Clears the data memory. (☞ Page 78)
6 :	Initializing set values	Initializes all memory settings. (☞ Page 79)
7 :	Printer connection, test print	Performs a test print. (☞ Page 80)

Note

- In the check mode, it is possible to return to the Measurement mode by pressing the MEAS key.

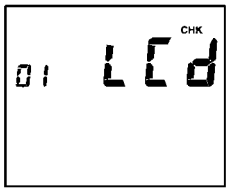
6.9.1 LCD check

All LCD segments are displayed.

(☞ Page 25)

1. Press the **SET** key in the Clock Display mode.

LCD check mode screen is displayed.



2. Press the **ENT** key.

3. Check to see if all LCD segments are displayed.

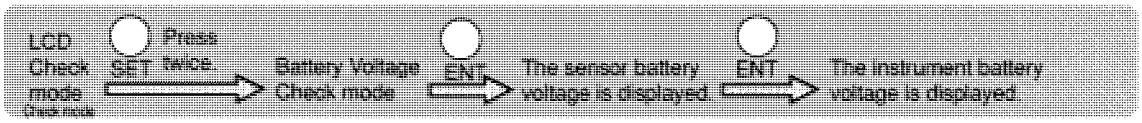
4. When the **SET** key is pressed, the instrument goes to the battery voltage check.

Note

- When the MEAS key is pressed, the instrument returns to the Clock Display mode.

6.9.2 Battery voltage check

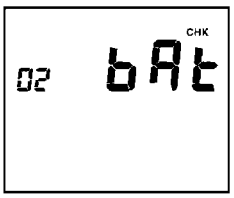
The battery voltage in use is displayed.



(☞ Page 73)

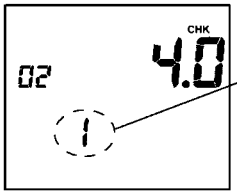
1. Press the **SET** key twice in the LCD Check mode.

Battery Voltage Check mode screen is displayed.



2. Press the **ENT** key.

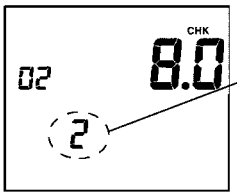
The sensor battery voltage is displayed.



1: Sensor battery voltage
Criteria
3.0 to 5.0 V : Normal
Less than 3.0 V: Replace the battery.
(Error No. 2 will blink.)

3. Press the **ENT** key.

The instrument battery voltage is displayed.



2: Instrument battery voltage
Criteria
5.5 to 11.0 V : Normal
Less than 5.5 V : Replace the battery.
(Error No.3 will blink.)

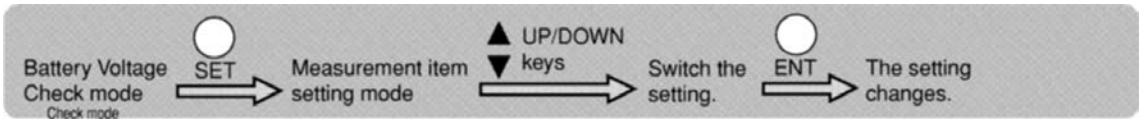
4. When the **SET** key is pressed, the instrument goes to the measurement item setting.

Note

- When the MEAS key is pressed, the instrument returns to the Clock Display mode.

6.9.3 Measurement item setting

Measuring items can be set.



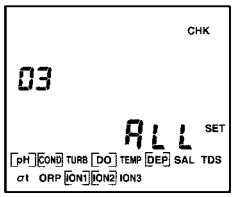
(☞ Page 73)

1. Press the **SET** key in the Battery Voltage Check mode.

Display setting mode screen is displayed.

2. Use the **UP/DOWN** (▲ ▼) keys to switch the measurement item.

The selected item blinks.



3. Press the **ENT** key to switch between [set/ not set] for the blinking item.

An item for which "set" is selected is indicated with [ ].

Note

- If the temperature is "not set" data for each component is not temperature-compensated and is displayed as data at 25 °C.

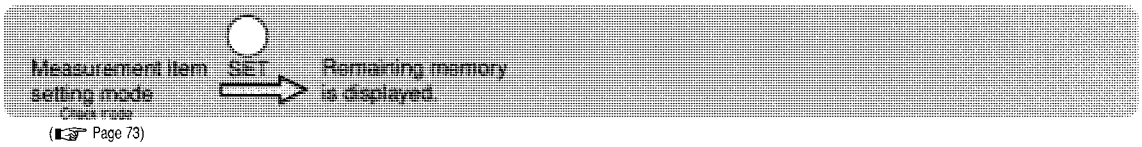
4. When the **SET** key is pressed, the instrument goes to the remaining memory display.

Note

- When the MEAS key is pressed, the instrument returns to the Clock Display mode.

6.9.4 Remaining memory

The number of date that can be stored can be displayed.



(☞ Page 73)

Press the **SET** key in the Display Setting mode.

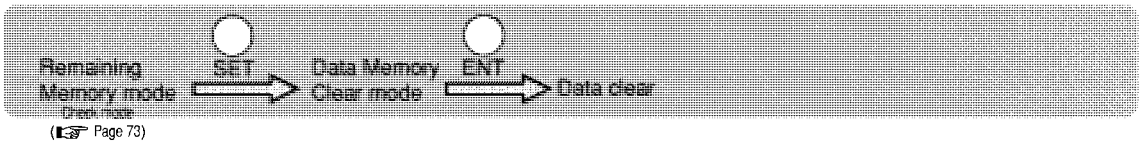
Remaining memory is displayed.

Note

- When the **SET** key is pressed, the instrument goes to the Data Memory Clear mode.
- When the MEAS key is pressed, the instrument returns to the Clock Display mode.

6.9.5 Data memory clear

All the data memory is cleared.



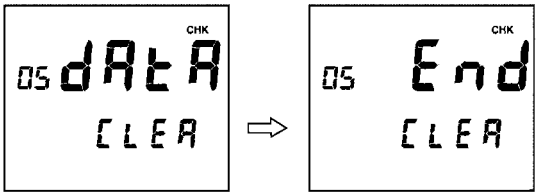
(☞ Page 73)

1. Press the **SET** key in the Remaining Memory mode.

Data memory clear mode screen is displayed.

2. Press the **ENT** key.

The data is cleared.



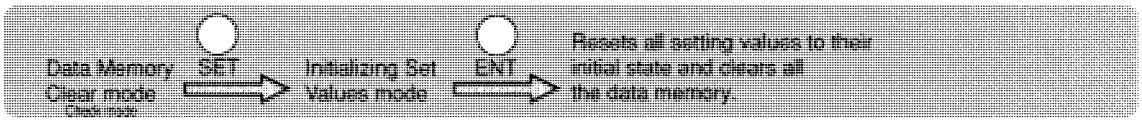
3. When the **SET** key is pressed, the instrument goes to the Memory Initialization mode.

Note

- When the MEAS key is pressed, the instrument returns to the Clock Display mode.

6.9.6 Initializing set values

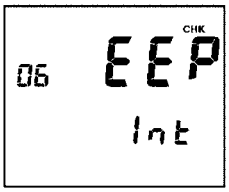
All setting values are reset to their initial state.



(☞ Page 73)

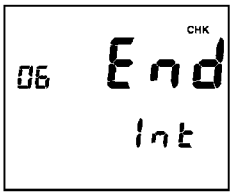
1. Press the **SET** key in the Data Memory Clear mode.

Initializing Set Values mode screen is displayed.



2. Press the **ENT** key.

All setting values are reset to their initial state.



3. When the **SET** key is pressed, the instrument goes to the Printer Connection mode.

Note

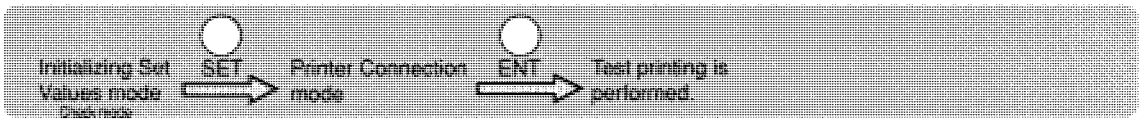
- When the MEAS key is pressed, the instrument return to the Clock Display mode.
- Data stored in the memory remains.

Initial setting

Item	Description	Initial value
Common	Display setting	Standard
	Data storage	Manual
pH	Unit	pH
COND	Unit	S/m
	Temperature coefficient	2.0 %/°C
DO	Salinity setting	AUTO
	Atmospheric pressure setting	1013 hPa
	Unit	mg/L
TURB	Unit	NTU
DEP	Unit	m
TDS	Coefficient	AUTO
σ_t	Unit	σ_t

6.9.7 Printer connection, test print

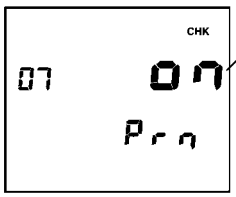
This mode only operates when the function expansion unit is connected. A test print is performed if a printer is connected.



(☞ Page 73)

1. Press the **SET** key in the Initializing Set Values mode.

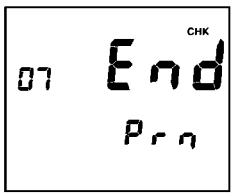
Printer Connection mode screen is displayed.



Displayed as OFF when not connected.

2. Press the **ENT** key to start printing.

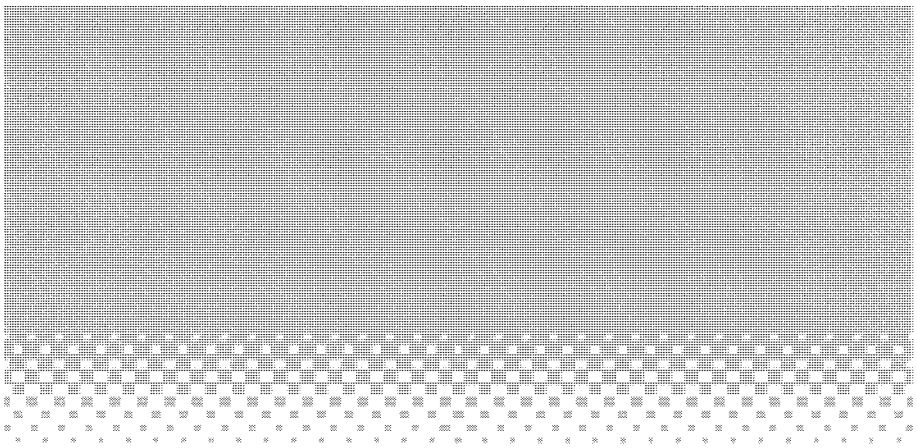
Normally, "End" is displayed. If an error has occurred, "Err" is displayed.



3. When the **SET** key is pressed, the instrument will return to the first LCD check mode.

◖Note◗

- When the MEAS key is pressed, the instrument returns to the Clock Display mode.



7. Instrument specifications

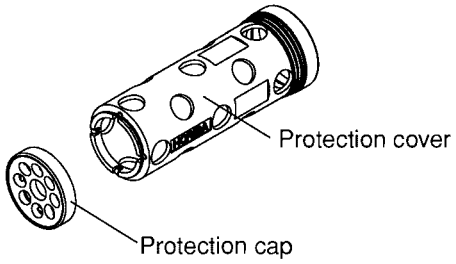
7.1 Daily maintenance

Sensor probe

● Storage method

After use, wash out with tap water and wipe off all contamination. Pour about 20 mL of pure water into the probe cap, install it on the sensor probe, and store in the carrying case.
In order to use the instrument regularly for a long time, store it after wiping off all contamination from the cable, sensor probe, and sensors.

Remove the protection cover once and completely wash out with tap water the left over sample on the screws. Reinstall the cover after having wiped off the drops of water. If there is any sample (especially sea water) left over on the screws, rust may form which may prevent the protection cover from being removed. (☞ Installation procedure, page 18.)
Depending on the level of contamination, remove the rubber protection cap from the tip of the protection cover and wash out with tap water. Reinstall it after wiping off the drops of water.

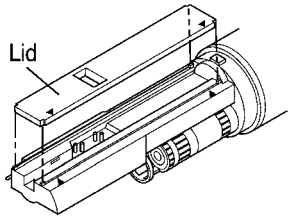


When storing with the pH/ORP and DO sensors attached to the probe, make sure to install the probe cap after having poured pure water into it.
Letting the pH/ORP and DO sensors get dry may cause deterioration of the instrument's performance. Should the sponge inside the probe cap be contaminated, replace it with a clean sponge (included).

TEMP/COND/TURB units

● To remove contamination

1. Remove the lid from the cell.
2. Clean the unit in tap water. If the unit is severely contaminated, use an absorbent cotton to remove contamination.
3. Attach the lid to the cell block before storage. (☞ page 29)



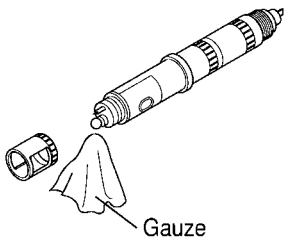
Important

- The cell has a window for turbidity measurement. Be careful to avoid damage to the window. In case of measurements, attach the lid to the cell in the correct direction.
- Don't remove the COND/TURB lid during calibration or measurement.
- Attach the lid to the cell with fitting four corners and facing ▲ marks each other.

pH/ORP sensors

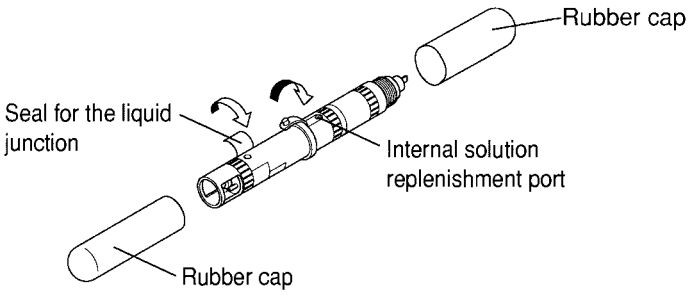
● To remove contamination

Use a piece of gauze dampened with detergent and wipe off contamination.



● Long-term storage

Remove the sensor from the sensor probe and check the internal solution replenishment port is closed. Then, attach a seal to the liquid junction and attach the rubber caps before storage.



● Monthly maintenance

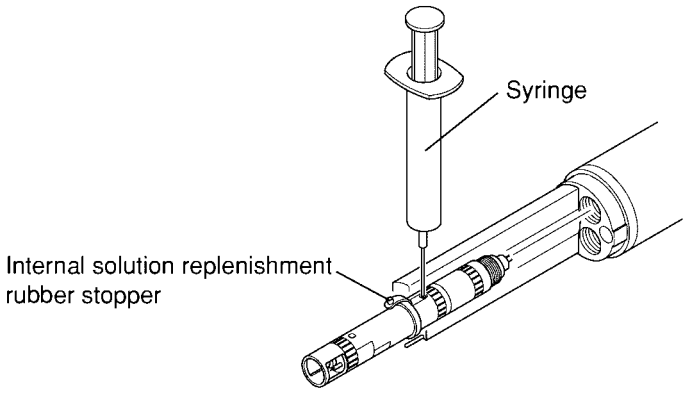
Replace the internal solution as described below:

1. Remove the sensor from the sensor probe using a sensor spanner.
2. Open the internal solution replenishment rubber stopper and remove the internal solution with a syringe.
3. Pour new internal solution (#330) to the level near rubber stopper. Be careful to avoid air bubbles from coming in the solition.
   Air bubbles in the internal solution will impair the sensors' pressure compensation function.

Important

- Shake the sensor to avoid bubbles in the internal solution from remaining at the bottom of the sensor.

4. Attach the sensor to the sensor probe.



DO sensor

● To remove contamination

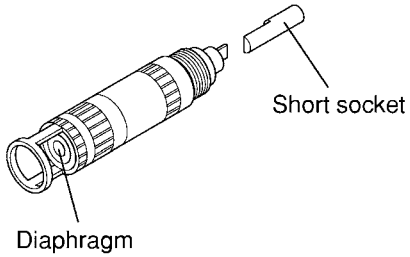
Wipe off contamination with gauze to avoid damage to the diaphragm.

● Long-term storage

Remove the sensor from the sensor probe using a sensor spanner. Set the supplied short socket and store the sensor in a cool(0 to 10℃), dark place.

Important

- Provide the DO sensor with a short socket or connect the sensor to the sensor probe for storage. Otherwise, the sensor may have a shorter life or stable instructions may not be obtained.
- The short socket is used when storing. Do not throw it away.



● Resetting the DO sensor when storing without having installed the short socket.

When leaving the DO sensor unattended for a brief period (1 or 2 days) without the short socket, the DO sensor can be reset by connecting it to the short socket or the probe. However, an amount of time corresponding to the period it was left unattended is necessary. If left unattended without being connected to the short socket or the probe for a long period (1 month), it cannot be reset.

● To replace the diaphragm.

Please read the instruction manual of the DO diaphragm replacement kit. (☞ page 89)

7.2 Troubleshooting

The instrument has a simple error message that informs users of operational errors and failure. Err No. is displayed at the bottom of the screen.

● Error message list

Err No.	Designation	Err No.	Designation
1	Sensor memory failure	6	Span calibration error
2	Sensor battery voltage drop	7	Calibration stability error
3	Instrument battery voltage drop	8	Printer error
4	Communications error	9	DATA IN error
5	Zero calibration error		

● Error and remedy

Important

- For err Nos. 5 to 7, the calibration err display disappears when a proper calibration is performed after the following action, or when the instrument is turned on again. For the other err Nos., the err display disappears after any of the following actions is taken.
- Error Nos. 2 and 3 are displayed even when using the AC adapter if the sensor probe battery voltage or instrument battery voltage drops is low on voltage.

Err NO.	Problem	Cause	Remedy
1	No data can be read from or written into the sensor probe memory.	Internal IC failure	Call your nearest store for sensor probe repair.
2	Sensor probe battery voltage drop	① Battery voltage drop ② Improper installation of the battery	① Replace the sensor probe battery. ② Set the batteries (LR03) in the correct direction.
3	Instrument battery voltage drop	① Battery voltage drop ② Improper installation of the battery	① Replace the instrument battery. ② Set the battery (6LR61) in the correct direction.
4	No communications possible between the instrument and the sensor probe	① Improper connection of the connector to the instrument ② Cable disconnection	① Connect the connector to the instrument properly and turn on the instrument again. ② Call your nearest store for cable repair.
5	No zero calibration possible	pH • The standard solution is contaminated. • Contamination on the pH glass membrane • Change in concentration of the internal solution for the reference electrode • Cracks in the pH glass electrode COND • The standard solution is contaminated. • The sensor is dirty. • The COND sensor is broken.	pH • Change the standard solution. • Clean the pH glass membrane. • Replace the internal solution for the reference electrode. • Replace the sensor. COND • Change the standard solution. • Clean the sensor. • Contact your nearest store.

Err NO.	Problem	Cause	Remedy
5	Zero calibration not possible	TURB	TURB
		• Air bubbles in the cell	• Swing the sensor probe while drawing a large arc.
		• Cell contamination	• Clean the cell.
		DO	DO
		• Damage to the diaphragm of the DO sensor	• Check the sensor and replace it if damaged.
		DEP	DEP
		• Contamination on the DEP sensor	• Clean the DEP sensor.
		• Damage to the DEP sensor	• Contact your nearest store.
6	Span calibration not possible	pH	pH
		• Contamination on the pH glass membrane	• Clean the pH glass membrane.
		• Change in concentration of the internal solution for the reference electrode	• Replace the internal solution for the reference electrode.
		• Cracks in the pH glass electrode	• Replace the sensor.
		• Damage to the connector pin	• Replace the sensor.
		COND	COND
		• The standard solution isn't correct.	• Calibrate with correct standard solution.
		• The standard solution value is set uncorrectly.	• Delete the calibration data for the conductivity, then calibrate the sensor again. (☞ Page 50)
		• The COND sensor is broken.	• Contact your nearest store.
		TURB	TURB
		• Air bubbles in the cell	• Swing the sensor probe while drawing a large arc.
		• Cell contamination	• Clean the cell.
		• The lid is attached uncorrectly.	• Confirm if the lid is attached correctly, then calibrate the sensor again. (☞ Page 29)
		DO	DO
		• Damage to DO sensor diaphragm	• Check the DO sensor and replace it if damaged.
		• DO sensor is unstable.	• Connect DO sensor to the sensor probe. Calibrate the sensor again 1 day later.
		• Damage to the connector pin	• Replace the sensor.
		DEP	DEP
		• Contamination on the DEP sensor	• Clean the DEP sensor.
		• Damage to the DEP sensor	• Contact your nearest store.
		TEMP	
		• Damage to the TEMP sensor	• Contact your nearest store.
7	The calibration value does not become stable within approximately three minutes.	① Sensor contamination	① Clean each sensor.
		② Dry sensor surface	② Pour the standard solution into the calibration beaker. Calibrate the sensor again 1 to 2 hours later.
		③ Severe temperature change	③ Calibrate the sensor in a place at a stable temperature or in a thermostatic oven.

Err NO.	Problem	Cause	Remedy
8	Printer unit failure		Turn OFF the instrument and use the remedy described below. Then turn ON the printer again.
		① Paper has jammed in the printer	① Remove the jammed sheet of paper
		② Improper printer unit connection	② Check to see if the printer is properl connected to the instrument.
		③ Printer failure	③ Replace the printer.
			* Contact your nearest store if the instrument does not recover after replacement of the printer.
9	Data cannot be stored because the memory is full.	No free space in the memory	Delete the data stored in the memory. (☞ Page 78)

● Other troubles

Remedies for various trouble with no Err No. displayed are described below.

Problem	Cause	Remedy
No data display with the power on	• No batteries	• Set new batteries.
	• Improper position of the positive and negative poles	• Set the batteries properly while paying attention to the positive and negative poles.
	• Battery voltage drop	• Replace the batteries with new ones.
	• Improper instrument battery contact	• Use radio pliers to narrow the positive terminal of the battery snap.
No setting change possible	• Automatic data storage is under way	• Press the CAL key to stop the automatic data storage.
No key operation possible	• The key lock function is working	• Turn OFF the instrument. Then turn ON the instrument again. (☞ Page 73)
	• Failure to calibrate the sensor or wrong calibration.	• Calibrate the sensor properly.
Blinking measured value	• Improper measurement sample	• Use a sample that is in the measurement range.
	• Sensor contamination	• Clean each sensor.
	• Poor calibration is possible. (The standard solution is contaminated.)	• Carry out correct calibration.
tYPE Err The Err is displayed and the operation cannot be performed.	• Improper connection of the cable connector to the instrument	• Connect the connector to the instrument properly and turn on the instrument again.
	• Cable disconnection	• Contact your nearest store.
	• Instrument inside failure	• Contact your nearest store.

● Troubleshooting for the TURB sensor

If an abnormal value such as -10, 800 or more is indicated, or indication does not become stable, follow as below instructions.

Remove the contamination of the sensor

Remove the cover of the turbidity (TURB) sensor, and clean the sensor with cotton swab.
Contamination or bubbles on the sensor may cause fluctuation of TURB values.

Remove bubbles around the sensor

When immersing sensor in the calibration cup, be sure lower it slowly. Quick immersion may cause bubbles on the sensor, which can have bad influence on calibration accuracy to give abnormal value indication.

Use of new standard solution

When calibration, clean the sensor before immersing it in the new standard solution. In case of zero calibration, when the standard solution is turbid or contaminated, calibrate again with the new standard one.

Points to be noted in making measurement

Immerse the sensor slowly in the sample. In case of abnormal measurement value observed, contamination or bubbles adhering may be suspected. So, shake greatly the sensor. Since immersion of the sensor in the sludge layer at the bottom of the sample can prohibit accurate measurement, shake greatly enough to remove the sludge.

● Maintenance of DO sensor

Durable life of DO sensor is generally one year, however, it may vary depending on the using condition. In case of the failure of calibration or breakage of the diaphragm, take either of the following steps according to the using period.

Within one year after purchasing :

Obtain diaphragm replacement kit (optional) to replace the used diaphragm and replenish the internal solution for restoration.

When exceeding one year after purchasing :

Replace by the new DO sensor.

● Materials

#5460 DO Sensor Diaphragm Replacement Kit Operation Manual

This operation manual explains how to replace the DO Sensor (#5460) Diaphragm.

1 This kit comes with the following.

● Diaphragm sheets	10 sheets
● Diaphragm retaining ring	5 pcs.
● O-ring (S9)	5 pcs.
● Internal solution #305 (50 mL)	1 bottle
● Diaphragm retaining plate	1 pc.
● Replacement stand	1 pc.
● Syringe and needle	1 set
● Operation manual	1 sheet

2 Diaphragm Replacement

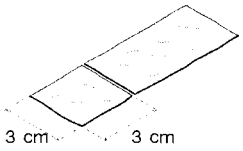
Chemical solution

Caution

The internal solution contains pottasium hydroxide (KOH) solution of high concentration.
If the solution comes in contact with hands or skin, wash immediately with water. If the solution comes in contact with the eyes, flush with ample amounts of water, then seek medical assistance.

1 Cut a diaphragm sheet to about 3 x 3 cm in size.

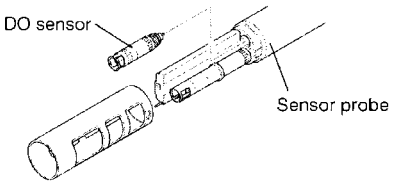
Note▶▶▶ Don't get any fingerprints or dust on the center part of the square.



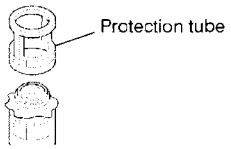
2 Detach the DO sensor from the sensor probe.

Ref▶▶▶ Refer to the U-21.22.23 Operation Manual, section 2.3.2 "Sensor Installation".

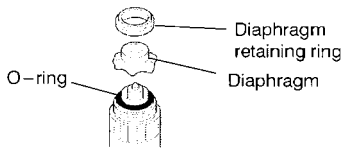
Note▶▶▶ If the short socket is not attached, instability may be seen when the sensor is used again.
Wear vinyl work gloves when handling the sensor. The KOH inside it is a strong alkaline and can irritate skin.



3 Detach the protection tube that holds the diaphragm in place. If it is difficult to remove, use some spanner, etc. to remove it.

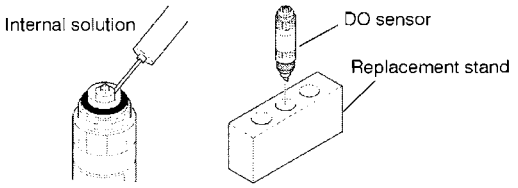


4 Detach the diaphragm retaining ring and diaphragm. Detach the diaphragm retaining ring and diaphragm if damaged or no longer functional.

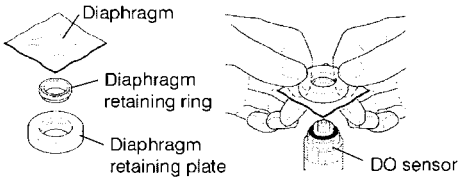


5 Set the sensor in the replacement stand ,and fill the internal solution with the attached syringe until the sensor tip is soaked with the solution.

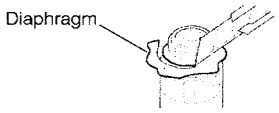
Note▶▶▶ Use the internal solution included in the kit for best performance.
In case some white crystals are seen, wipe them out completely with a Kimwipe®, etc.
In case the internal solution includes white crystals, remove the internal solution and fill up again. If the white crystals cannot be seen, just fill up.



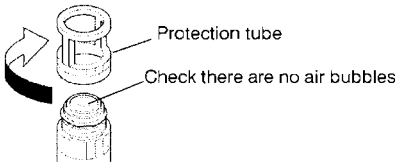
6 Fit the diaphragm retaining ring into the diaphragm retaining plate. Then, lay the diaphragm over the sensor and carefully cover with the ring and plate so that the diaphragm does not wrinkle. Finally, remove the retaining plate.



7 Cut the draped edge of the diaphragm to the shape of the sensor.

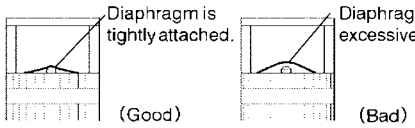


8 Check there are no air bubbles inside the sensor and tighten the protection tube securely.



9 Check the diaphragm bulges upward as shown on the below left and that it is not wrinkled.

Note▶▶▶ Check that span calibration can be made correctly. Sensitivity lowers and response speed slows if the diaphragm does not bulge sufficiently.



For any question regarding this product, please contact your local agency, or inquire from the Customer Registration website (www.horiba.co.jp/register).

HORIBA, Ltd.

7.3 Specifications

NOTE ○: Applicable
—: Unapplicable

		U-22XD
Instrument	Water-proof construction	IP67
	Mass	Approximately 500 g (including the grip holder)
Sensor *1	Use in 2-inch well	○
	Measurement temperature	0 to 55 °C
	Storage temperature	-5 to 60 °C
	Measurement depth	to 100 m
	Maximum sensor outside diameter	47 mm
	Sensor length	380 mm
	Continuous use available *2	30 days
	Automatic data gathering at set time	○
	Mass (Cable10 m)	Approximately 1.9 kg
pH ● Two-point calibration ● Automatic temperature compensation	Measuring principle	Glass electrode method
	Range	pH0 to 14
	Resolution	0.01 pH
	Repeatability	±0.05 pH
	Accuracy	±0.1 pH
Dissolved-Oxygen ● Salinity conversion (0 to 40 ppt/Auto) ● Automatic temperature compensation	Measuring principle	Diaphragm galvanic battery method
	Range	0 to 19.99 mg/L
	Resolution	0.01 mg/L
	Repeatability	±0.1 mg/L
	Accuracy	±0.2 mg/L
Conductivity ● Auto range ● Automatic temperature conversion (25 °C)	Measuring principle	4 AC electrode method
	Range	0 to 9.99 S/m
	Resolution	0.1 % of full scale
	Repeatability	±1 %
	Accuracy	±3 %
Salinity	Measuring principle	Conductivity conversion
	Range	0 to 4 %
	Resolution	0.01 %
	Repeatability	±0.1 %
	Accuracy	±0.3 %
Total Dissolved Solid(TDS) ● Conversion factor setting	Measuring principle	Conductivity conversion
	Range	0 to 99.9 g/L
	Resolution	0.1 % of full scale
	Repeatability	±2 g/L
	Accuracy	±5 g/L
Seawater specific gravity ● Display σ_t, σ_0, σ_{15}	Measuring principle	Conductivity conversion
	Range	0 to 50 σ_t
	Resolution	0.1 σ_t
	Repeatability	±2 σ_t
	Accuracy	±5 σ_t
Temperature	Measuring principle	Thermistor method
	Range	0 to 55 °C
	Resolution	0.01 °C
	Repeatability	±0.3 °C
	Accuracy	±1.0 °C

		U-22XD
Turbidity (TURB)	Measuring principle	Penetration and scattering method
● Unit selection	Range (NTU or mg/L)	0 to 800 NTU
	Resolution	0.1 NTU
	Repetability	±3 %
	Accuracy	±5 %
Water depth	Measuring principle	Pressure method
	Range	0 to 100 m
	Resolution	0.1 m
	Repetability	±3 %
	Accuracy	±5 %
Oxidation-reduction potential (ORP)	Measuring principle	Platinum electrode method
	Range	± 1999 mV
	Resolution	1 mV
	Repetability	± 5 mV
	Accuracy	±15 mV
Simultaneous measurement items		10

Note: The accuracy rating value is obtained from measurements at intermediate point of the standard solution after two-point calibration (at room temperature and pressure). The repeatability and accuracy rating percentages are based on the full scale (except for salinity).

*1: Organic solvents, strong acids, and strong alkaline solvents cannot be measured.

*2: Based on the data measured automatically at 15 minutes intervals. The battery life taken into account. Periodical maintenance and calibration is necessary when a lot of shellfishes and seaweeds exist at the measurement point.

7.4 Spare parts

Sensors

Sensor	Model	Spare part number
pH sensor	6230	9037-0056-00
pH/ORP sensor	6280	9037-0057-00
DO sensor	5460	9037-0058-00

Standard and internal solutions

Solution	Model	Spare part number	Remark
pH 4 standard solution (500 mL)	100-4	9003-0016-00	Standard solution for AUTO calibration, which is in addition used for manual pH span calibration.
pH 7 standard solution (500 mL)	100-7	9003-0017-00	Standard solution for pH zero calibration
pH 9 standard solution (500 mL)	100-9	9003-0018-00	Standard solution for manual pH span calibration
Powder for ORP standard solution (250 mL × 10)	160-51	9003-0031-00	Powdered standard solution to be used for checking ORP behavior
Powder for ORP standard solution (250 mL × 10)	160-22	9003-0030-00	
pH reference internal solution (250 mL)	330	9037-0052-00	Replenishment internal solution for pH reference electrode

Others

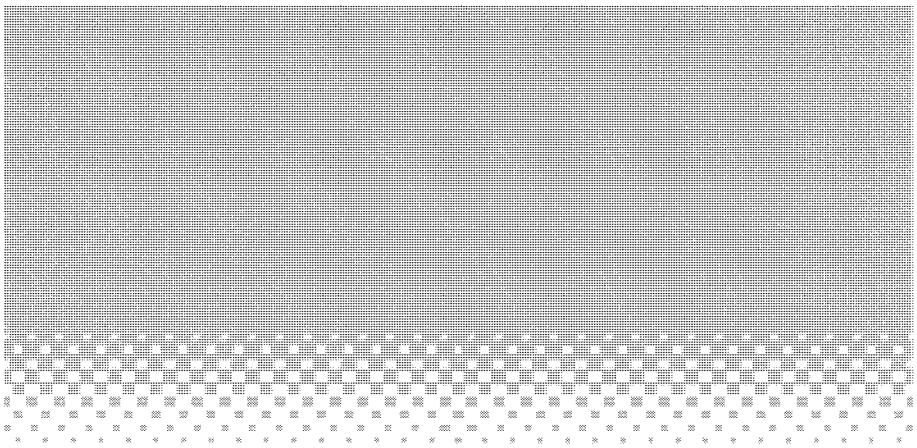
	Model	Spare part number	Remark
Calibration beaker XD	–	9037-0086-00	This is similar to the standard accessory, and used for sensor calibration.
Connector plug for the prove	–	9037-0071-00	When using the probe separately from the instrument, this is used to maintain waterproof of the connector.
Sensor spanner	–	9037-0088-00	This is used to connect the sensor to the probe. Similar to the standard accessory.
DO diaphragm replacement kit	–	9037-0074-00	In case of breakage of the DO sensor diaphragm, it is used in the replacement of the diaphragm to restore the sensor.
Battery cover packing	–	9096-0013-00	Replacement packing to be used for battery box of the main unit.
System unit cover O-ring	–	9096-0014-00	Replacement packing to be used for EXT cover of the main unit.
Sensor O-ring	–	9037-0076-00	Replacement O-ring to be used for connector of pH/ORP sensor and Do sensor.
Probe cap XD	–	9037-0087-00	This cap is to be used when storing the sensor probe.
Battery caver O-ring	–	9037-0084-00	This replacement O-ring is used for the sensor probe's battery cover.
Silicon grease	–	9037-0085-00	This silicon grease is applied on the sensors' O-rings. Similar to the standard accessory.
Protection cover packing	–	9037-0091-00	This is packing for when taking off the probe cap and seal after installing the protection cover. (board packing and O-ring set)
Sponge	–	9037-0089-00	This replacement sponge is used for the probe cap XD.
Protection cap	–	9037-0090-00	This cap is to be attached to the protection cover.

* The spare parts above are prepared by dealers.
Order the part by designating the parts name, model and spare parts number.

7.5 Option

Parts name	Model	Remark
Expansion adaptor	U-2001	This is applicable to AC adapter connection, RS-232C communication, GPS connection, printer output, and data-collecting software.
System unit *	U-2002-100V U-2002-110V U-2002-220V	This is applicable to AC adapter connection, RS-232C communication, GPS connection, printer output, and data-collecting software. GPS and printer are included in a complete set.
AC adaptor (for 100 V)	AC-10	AC adapter intended to drive the U-20 series by AC power supply. This should be used together with U-2001 and U-2002.
Carrying case	W-2010	Compact carrying case for cable below 10 m in length . Not large enough to hold flow cell or guard.
Carrying case	W-2030	Bigger-sized carrying case for cable exceeding 30 m in length. Large enough to hold flow cell.
Flow cell	W-2100	To be used for measurement at a pumping up sample.
Probe guard	W-2200	To be used for measurement at a location where there is a flow or a location with a thick sludge layer residing at the bottom.
PC connection cable	—	Nine-pin connection cable to PC.

* Specify the power source and voltage of the printer when ordering.



8. Reference Data

● pH measurement

1. Principle of pH measurement

U-20XD series use the glass electrode method for pH measurements. The glass electrode method measures a potential difference between the glass film for pH and the comparison electrode. For more information, refer to JIS Z 8802 pH measurement method.

2. Temperature compensation

The electromotive force generated by the glass electrode changes depending on the temperature of the solution. Temperature compensation is used to compensate for the change in electromotive force caused by temperature.
This function does not compensate the change in pH caused by the temperature of the solution. When pH is to be measured, the temperature of the solution when the pH is measured must be recorded along with that pH value, even if a meter that has automatic temperature compensation is used. If the solution temperature is not recorded, the results of the pH measurement may be meaningless.

3. Types of standard solutions

When measuring pH, the pH meter must be calibrated using a standard solution. There are five kinds of standard solutions specified in "JIS 28802 pH measurement". For normal measurement, two of standard solutions with a pH of 4, 7, and 9 are sufficient to accurately calibrate the meter.
For standard solutions, refer to "JIS Z 8802 pH measurement".

pH 4 standard solution ..... 0.05 mol/L potassium hydrogen phthalate aqueous solution
(Phthalate)
pH 7 standard solution ..... 0.025 mol/L potassium dihydrogenphosphate, 0.025 mol/L sodium phospate aqueous solution
(Neutral phosphate)
pH 9 standard solution ..... 0.01 mol/L tetra-sodium boric acid aqueous solution
(Borate)

pH values of pH standard solutions at various temperatures settings.

Temp. (°C)	pH 4 standard solution Phthalate	pH 7 standard solution Neutral phosphate	pH 9 standard solution Borate
0	4.01	6.98	9.46
5	4.01	6.95	9.39
10	4.00	6.92	9.33
15	4.00	6.90	9.27
20	4.00	6.88	9.22
25	4.01	6.86	9.18
30	4.01	6.85	9.14
35	4.02	6.84	9.10
40	4.03	6.84	9.07
45	4.04	6.84	9.04

4. Supplements for pH measurement

Pressure compensation diaphragm

U-20XD series can measure pH with high accuracy through the pressure compensation diaphragm without being affected by hydraulic pressure. Attention should be paid to the following points so that the diaphragm may function fully.
Before measurement, use a syringe and fill the reference electrode up to the replenish port with the internal solution. When injecting the polarity reference internal solution, be careful that air bubbles do not get into the solution.

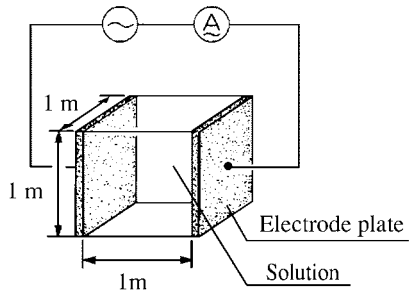
● COND measurement

1. Four-AC-electrode method

Conductivity is an index of the flow of electrical current in a substance.

Salts dissolved in water are separated into cations and anions. Such solution is called electrolytic solution. Electrolytic solution has the property of allowing the flow of current according to Ohm's law. This property is referred to as ionic conductivity, since current flow is caused by ion movement in electrolytic solution. Metals, on the other hand, allow the flow of current by means of electrons. This property is called electronic conductivity, which is distinguished from ionic conductivity.

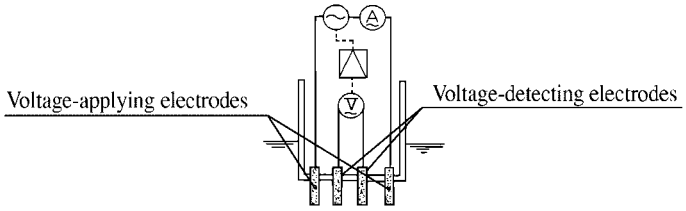
A cube with 1 m on each side, as shown in Fig. 1, is used to demonstrate an electrolytic solution. Two electrode plates are placed on opposite sides, and the cube is filled with a solution. If the resistance between these two electrode plates is represented by r (Ω), the conductivity of the solution L ($S.m^{-1}$) is represented as L=1/r. S stands for Siemens, a unit of measurement of conductance.



(Fig. 1 Definition of conductivity)

The most general method for measuring conductivity is based on the above principle, and is called the 2-electrode method. In the 2-electrode method the influence of polarization cannot be ignored for solutions with high conductivity and conductivity cannot be measure accurately. In addition, contamination on the surface of the electrode increases apparent resistance, resulting in inaccurate measurement of conductivity.

The U-20XD series has adopted the 4-electrode method to overcome these disadvantages of the the 2-electrode method. As shown in Fig. 2, the U-20XD series uses two voltage-detecting electrodes and two voltage-applying electrodes, for a total of four electrodes. The voltage-detecting electrodes are for detecting AC voltage, and the voltage-applying electrodes are for applying AC voltage.



(Fig. 2 Principle of the 4-electrode method)

Let us assume that the current, I (A), flows in a sample of conductivity L – under automatic control of the voltage-applying electrodes – so that the voltage at the voltage detecting-electrodes, E (V), remains constant at all times. Then, the resistance of the sample, R (Ω), across the voltage-detecting electrodes is represented as R=E/I. The resistance, R, of the sample is inversely proportional to its conductivity, L. Accordingly, a measurement of conductivity, Is, of a standard solution of known conductivity, Ls, enables calculation of conductivity of a sample according to the formula L = Ls (I/Is) from the ratio L : Ls = I : Is.

Even in the 4-electrode method, polarization occurs, since AC current flows in the voltage-applying electrodes. The voltage-detecting electrodes are, however, free from the effects of polarization, since they are separated from the voltage-applying electrodes, and furthermore, current flow is negligible. Therefore, the 4-electrode method is an excellent method to enable measurement of conductivity covering a very high range.

2. SI units

New measurement units, called SI units, have been in use from 1996. Accordingly, the U-20XD series also uses SI units. The following conversion table is provided for people who use the conventional kind of conductivity meter. Note that along with the change in unit systems, the measurement values and cell counts have also changed.

	Former units →	SI units
Measurement	0.1 mS/cm →	0.01 S/m
value	1 mS/cm →	0.1 S/m
	100 mS/cm →	10 S/m

3. Temperature coeffcient

In general, the conductivity of a solution varies largely with its temperature. The conductivity of a solution depends on the ionic conductivity, described earlier. As the temperature rises, conductivity becomes higher since the movement of the ions becomes more active. The temperature coefficient shows the change in % of conductivity per °C, with a certain temperature taken as the reference temperature. This is expressed in units of %/°C. The temperature coefficient assumes the premise that the conductivity of a sample changes linearly according to temperature. Strictly speaking, with actual samples, however, conductivity changes along a curve. Furthermore, the cuve varies with the type of sample. In the ranges of smaller temperature changes, however, samples are said to have the temperature coefficient of 2 %/°C (at reference tempreture 25 °C) this holds for most samples, except in certain special cases.
(The temperature coefficients for various types of solutions are listed on the next page.)
The U-20XD series uses an automatic temperature conversion function to calculate conductivity at 25 °C at a temperature coefficient of 2 %/°C, based on the measured value of the temperature. Results are displayed on the readout.
The U-20XD series's temperature conversion function is based on the following formula.

$$L_{25} = L_t / \{ 1 + K (t - 25) \}$$

L_{25} : Conductivity of solution converted to 25 °C
(value displayed on U-20XD series)
t : Temperature of solution at time of measurement (°C)
L_t : Conductivity of solution at t (°C)
K : Temperature coeffcient (%/°C)

Conductivity and temperature coefficient for various types of solutions

Conductivity and related temperature coefficients of representative substances (at 25 °C) are shown in the table below.

Substance	Concentration wt%	Conductivity S/m	Temperature coeffcient %/°C	Temperature °C
NaOH	5	19.69	2.01	15
	10	31.24	2.17	
	15	34.63	2.49	
	20	32.70	2.99	
KOH	25.2	54.03	2.09	15
	29.4	54.34	2.21	
	33.6	52.21	2.36	
	42	42.12	2.83	
NH_3	0.1	0.0251	2.46	15
	1.6	0.0867	2.38	
	4.01	0.1095	2.50	
	8.03	0.1038	2.62	
HCl	5	39.48	1.58	18
	10	63.2	1.56	
	20	76.15	1.54	
	30	66.20	1.54	
H_2SO_4	5	20.85	1.21	18
	10	39.15	1.28	
	20	65.27	1.45	
	40	68.00	1.78	
	50	54.05	1.93	
	60	37.26	2.13	
	100.14	1.87	0.30	
HNO_3	6.2	31.23	1.47	18
	12.4	54.18	1.42	
	31	78.19	1.39	
	49.6	63.41	1.57	
H_3PO_4	10	5.68	1.04	15
	20	11.29	1.14	
	40	20.70	1.50	
	45	20.87	1.61	
	50	20.73	1.74	
NaCl	5	6.72	2.17	18
	10	12.11	2.14	
	15	16.42	2.12	
	20	19.57	2.16	
	25	21.5	2.27	

Substance	Concentration wt%	Conductivity S/m	Temperature coeffcient %/°C	Temperature °C
Na_2SO_4	5	4.09	2.36	18
	10	6.87	2.49	
	15	8.86	2.56	
Na_2CO_3	5	4.56	2.52	18
	10	7.05	2.71	
	15	8.36	2.94	
KCl	5	6.90	2.01	18
	10	13.59	1.88	
	15	20.20	1.79	
	20	26.77	1.68	
	21	28.10	1.66	
KBr	5	4.65	2.06	15
	10	9.28	1.94	
	20	19.07	1.77	
KCN	3.25	5.07	2.07	15
	6.5	10.26	1.93	
NH_4Cl	5	9.18	1.98	18
	10	17.76	1.86	
	15	25.86	1.71	
	20	33.65	1.61	
	25	40.25	1.54	
NH_4NO_3	5	5.90	2.03	15
	10	11.17	1.94	
	30	28.41	1.68	
	50	36.22	1.56	
$CuSO_4$	2.5	10.90	2.13	18
	5	18.90	2.16	
	10	32.00	2.18	
	15	42.10	2.31	
CH_3COOH	10	15.26	1.69	18
	15	16.19	1.74	
	20	16.05	1.79	
	30	14.01	1.86	
	40	10.81	1.96	
	60	4.56	2.06	

● SAL conversion

The U-20XD series is designed to measure salinity as well as the other parameters.
Note that the "salinity" referred to here is the salinity of sea water. There is a constant relation between conductivity and salinity at certain temperatures.
Therefore, if data on the conductivity and temperature are available, the corresponding salinity is known. In other words, the salinity measurement of the U-20XD series is based on the principle of calculating the salt content, making use of the measured values of conductivity and temperature.
Note therefore, that measured results of all substances whose conductivity is detected are displayed as salinity. For example, the measured result is displayed as NaCl concentration, even if in fact the sample component is, for example, hydrochloric acid (HCl).

● TDS conversion

TDS is short for Total Dissolved Solids and means the total dissolved solid amount.
The conductivity of a solution is affected by the amount of salinity, minerals, and dissolved gases. That is, conductivity is an index that shows the total amount of all substances in the solution. Of these substances, TDS indicates only the amount of dissolved solids.
TDS can be used for a comparison of the state of substances composed of a single component such as NaCl. However, the use of TDS for the comparison of solutions of different types causes serious errors.
Conductivity and TDS are expressed by the following formulas:

Conductivity in SI units (S/m)	TDS(g/L) = L (S/m) × K × 10
	TDS(g/L) = L (mS/m) × K ÷ 100
Conductivity in the old units (mS/cm)	TDS(g/L) = L (mS/cm) × K
	K = TDS coefficient

Initial settings use the values listed in the table (☞ Page 70) that generally uses TDS coefficients.
For accurate TDS comparisons, find the TDS coefficient from measured conductivity values. Then set the value thus obtained and make measurements.

● σ_t conversion

Specific gravity of seawater

The density and specific gravity of seawater are equal numerically and generally are not distinguished strictly. Since seawater density ρ is between 1.000 and 1.031, 1 is subtracted from ρ and σ is obtained by multiplying the value by 1000.
The resultant value is used as the specific gravity of seawater.

$$\sigma = (\rho - 1) \times 1000$$

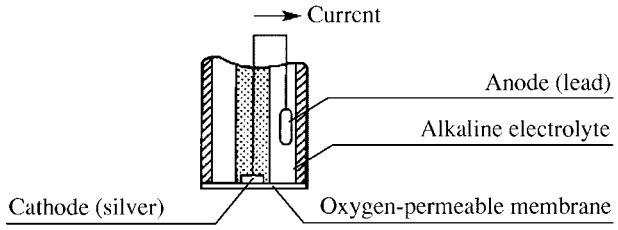
The density of seawater ρ is expressed by temperature, hydraulic pressure, and salinity functions. The density of seawater σ under the atmospheric pressure is expressed as σ_t. The density of seawater under the atmospheric pressure is determined by temperature and salinity.
The U-20XD series models make salinity measurement through temperature measurements and conductivity conversion and find σ_t through calculations.
In Japan σ_{15} at 15 °C is called a standard specific gravity and widely used while in foreign countries σ_0 at 0 °C is employed. σ_{15} and σ_0 are determined by the function of salinity.
In ocean surveys, in particular, these values σ_t, σ_{15}, and σ_0 are more widely used than conductivity and salinity and, in the U-20XD series models, newly added as measurement components.

● DO measurement

1. Principle of measurement

The "DO" referred to here means the concentration of oxygen dissolved in water. DO is essential to self-purification of river and sea and to water creatures such as fish. DO measurement is also essential to drainage and water quality control.

Fig. 3 shows the principle of measurement using a DO sensor.



(Fig. 3 Principle of DO sensor)

A noble metal (silver) is fitted closely to an oxygen-permeable membrane to make the cathode; a base metal (lead) is used as the anode. Both are immersed in an alkaline electrolyte with the anode-to-cathode external circuit closed. Oxygen diffusing through the oxygen-permeable membrane causes a reduction reaction at the cathode; this allows flow of current in the external circuit:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

At the anode, oxidation reaction occur as follows:

$$2Pb \rightarrow 2Pb2^+ + 4e^-$$

The current is proportional to the quantity of oxygen diffusing through the oxygen-permeable membrane. Accordingly, measurement of the current makes the DO in a sample known.

The DO measuring method based on this principle is called the membrane-electrode method. This method allows convenient measurement of DO, especially when compared with chemical-analysis method, which needs complicated pre-treatment to eliminate the effects of oxidizing or reducing substances.

2. DO correction for salinity

When a solution and air are in contact and in complete equilibrium (saturated), DO: C [mg/L] in the solution, and the oxygen partial-pressure: Ps [MPa] in air are in the following relation:

$$C = Ps/H$$

H [MPa/ (mg/L)] is referred to as Henry's constant, which depends on the composition of the solution. In general, C becomes smaller as the salinity in the solution increases, since H becomes larger.

A DO sensor is intended to detect Ps in the above expression. Therefore, the DO measurement would be in error if the DO sensor were immersed either in air-saturated pure water or in solution with salt. To settle this problem, it is necessary to correct the DO reading based on the salinity of the sample using salinity correction.

Conventional DO meters make this salinity correction by inputting a known salinity value. This poses no problems if the salinity of the sample is known. In general, however, the salinity of the sample is usually not known, and the method is not practical even if the DO meters are equipped with the salinity correction function.

The U-20XD series is capable of measuring the salinity of a sample and automatically correcting the using this function.

3. Features of the U-20XD series DO sensors

In conventional DO measurements, it was necessary to keep the velocity of the flow constant because the velocity of flow led to fluctuation in indicated values. In our U-20XD series models, improvements in sensors have made it possible to make measurements with stable indications and with little influence of the velocity of flow.

● Turbidity (TURB) measurement

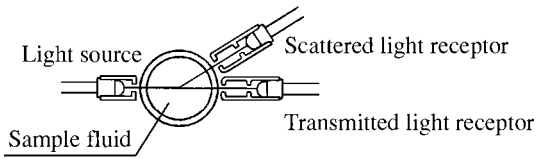
1. Principle of measurement

From among several types of turbidity-measuring methods available, the U-20XD series uses the light-transmission-scattering method, shown in Fig. 4.

Irradiation of a beam of light onto a sample brings about separation of the beam into (1) the light transmitted through the solution and (2) the light scattered by turbidity components in the sample. In the light-transmission-scattering method, the intensity of both transmitted light and the scattered light are measured using separate receptors, and the turbidity is obtained based on the ratio of the two.

With the U-20XD series, the light source is a pulse-lighting infrared-emission diode. The scattered light is measured at a point 60° offset from the light source. This light-absorption-scattering method has several advantages, including the fact that (1) the actual color of the sample fluid has little effect on the measurement of turbidity, (2) fluctuations in light quantity from the light source are easily compensated for, and (3) it allow the U-20XD series to be operated with relatively low-power consumption.

The turbidity value differs with the structure of the cell so changes with the instrument.



(Fig. 4 Principle of the light-transmission-scattering method)

2. Standard solution

U-20XD series can perform calibration using formazin (NTU) or kaolin standard solutions as a turbidity standard solution. However, units for the solution used for calibration should be displayed in measurements. Do not use more than 400 mg/L of kaolin standard solution because it increases precipitation speed, resulting in measurement error.

● DEP measurement

1. Depth (DEP) measurement

For the U-22XD model, depth measurement can be made through use of a pressure gauge. The principle of the depth measurement uses the relation between depth and pressure.

Although the measurement with the depth sensor is affected by atmospheric pressure, the depth sensor, however, makes zero-point adjustments through the automatic calibration before measurements.

2. Influence of temperature and calibration

The depth sensor depends greatly on temperature. For a wide difference between the temperature at which the sensor has been automatically calibrated and the temperature of the measurement sample, the sensor can make depth measurements with a higher accuracy by the following method:

Immerse the depth sensor of the sensor probe into the sample.

Keep the sensor immersed in the sample for approximately 30 minutes until the temperatures of the sensor and the sample are the same.

Then make the zero calibration of the sensor manually. (☞ Page 57)

● Measuring mV (oxidation-reduction potential (ORP))

ORP principles

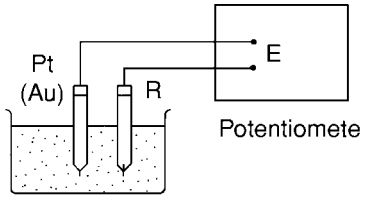
ORP (or "redox potential") is an abbreviation for oxidation-reduction potential. ORP is the energy level (potential) determined according to the state of equilibrium between the oxidants (M^{Z+}) and reductants $M^{(Z-N)+}$) that coexist within a solution.

$M^{z+} + ne^- \Leftrightarrow M^{(z-n)+}$.....①

If only ① exists within a solution, a metal electrode (platinum, gold, etc.) and a reference electrode are inserted into the solution, forming the ORP measuring system shown in Fig. 5. Measuring the potential (ORP) that exists between the two electrodes enables the potential to generally be expressed by the following equation.

$$E = E_0 - \frac{RT}{nF} \ln \frac{a_{M^{(z-n)+}}}{a_{M^{z+}}} \quad \text{..... ②}$$

E: Electric potential E_0 : Constant R : Gas constant T : Absolute temperature
n : Electron count F : Faraday constant a : Activity



(Fig. 5 Measuring mV)

For example, for a solution in which trivalent iron ions coexist with bivalent iron ions, equations ① and ② would be as follows.

$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$.....①

$$E = E_0 - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \quad \text{.....②}$$

When only one type of state of equilibrium 1 exists in the solution, the ORP of the solution can be determined uniquely by equation 2. What is important here is that ORP is determined by the ratio of activity between the oxidant (Fe^{3+}) and the reductant (Fe^{2+}) (using the equation $a_{Fe^{2+}}/a_{Fe^{3+}}$). Actually, however many kinds of states of equilibrium exist simultaneously between various kinds of ions, in most solutions. This means that under actual circumstances, ORP cannot be expressed using the simple equation shown above and that the physical and chemical significance with respect to the solution is not very clear.

In this respect, the value of ORP must be understood to be only one indicator of the property of a solution. The measurement of ORP is widely used, however, as an important index in the analysis of solutions (potentiametric titration) and in the disposal and treatment of solutions.

Recently, there have appeared various claims regarding this matter, such as that a high degree of ORP is effective in sterilization or that drinking water that has a low ORP reduces the chance of illness by reacting with the activated oxygen in the cells of the body. ORP is used as an index for alkaline drinking water.

Standard electrode (reference electrode) types and ORP

The ORP of a solution that is obtained through measurement is a value that corresponds to the reference electrode employed.
If different kinds of reference electrodes are used for measurement, the ORP value of the same solution may appear to be different. HORIBA uses Ag/AgCl with 3.33 mol/L KCl as the reference solution for reference electrodes. According to general technical literature, standard hydrogen electrodes (N.H.E.) are often used as the standard electrode.
The relationship between N.H.E. and the ORP that is measured using an Ag/AgCl with 3.33 mol/L KCl electrode is expressed by the following equation.

$E_{N.H.E.} = E + 206 - 0.7\,(t - 25)mV \qquad t = 0 - 60\,℃$

$E_{N.H.E.}$: Measured ORP value using N.H.E. as the reference electrode

E: Measured ORP value using Ag/AgCl with 3.33 mol/L KCl as the reference electrode

Potential sign

Standard ORP is expressed in the following way, in literature related to electrochemistry and analytical chemistry.

A $Li^+ + e^- \rightarrow Li$

E0=-3.024 V VS N.H.E.

However, in some literature, the "+" and "-" signs are reversed.

B $Li \rightarrow Li^+ + e^-$

E0=+3.024 V VS N.H.E.

In expressions like B, above, the reaction is just reversed and there is no essential difference. But this kind of expression does invite confusion. The majority of the world, today, is consistent in its use of the signs as they are used in A, above. For this reason, HORIBA, too, uses signs concerning ORP that are consistent with A, above.

表 3

For any question regarding this product,
please contact your local agency,
or inquire from the Customer Registration
website (www.horiba.co.jp/register).

HORIBA, Ltd.

First edition: November 2001
CODE : 11000908000

2020
TURBIDIMETER

Instruction MANUAL

TABLE OF CONTENTS

GENERAL INFORMATION

PACKAGING & DELIVERY

Experienced packaging personnel at LaMotte Company assure adequate protection against normal hazards encountered in transportation of shipments. After the product leaves the manufacturer, all responsibility for safe delivery is assured by the transportation company. Damage claims must be filed immediately with the transportation company to receive compensation for damaged goods.

Should it be necessary to return the instrument for repair or servicing, pack the instrument carefully in a suitable container with adequate packing material. A return authorization number must be obtained from LaMotte Company by calling 1-800-344-3100 or faxing 1-410-778-6394. Attach a letter with the authorization number to the shipping carton which describes the reason for the return. This information will enable the service department to make the required repairs more efficiently.

GENERAL PRECAUTIONS

Read the instruction manual before attempting to set up or operate this instrument. Failure to do so could result in personal injury or damage to the instrument.

The 2020 Turbidimeter should not be stored or used in a wet or corrosive environment. Care should be taken to prevent water from wet turbidity tubes from entering the turbidimeter light chamber.

NEVER PUT WET TUBES IN THE TURBIDIMETER.

SAFETY PRECAUTIONS

Read the label on all reagent containers. Some labels include precautionary notices and first aid information. Certain reagents are considered hazardous substances and are designated with a * in the instruction manual. Material Safety Data Sheets (MSDS) are supplied for these reagents. Read accompanying MSDS before using these reagents. Additional emergency information for all LaMotte reagents is available 24 hours a day from the Poison Control Center listed in the front of the phone book. Be prepared to supply the name and four digit LaMotte code number found on the container label or at the top of the MSDS. LaMotte reagents are registered with a computerized poison control information system available to all local poison control centers.

LIMITS OF LIABILITY

Under no circumstances shall LaMotte Company be liable for loss of life, property, profits, or other damages incurred through the use or misuse of their products.

SPECIFICATIONS

Instrument Type	Nephelometric turbidity, calibrated in NTU
Range	0.00 -1100 NTU
Accuracy	.05 or ±2% for readings below 100 NTU, whichever is greater ±3% above 100 NTU
Resolution	*Standard Mode* 0.01 from 0.00 -10.99 NTU 0.1 from 11.0 -109.9 NTU 1 from 110 -1100 NTU *EPA Mode* NTU — Reported to the nearest NTU 0 - 1.0 — 0.05 1.0 - 10 — 0.1 10 - 40 — 1 40 - 100 — 5 100 - 400 — 10 400 - 1000 — 50 1000 — 100
Display	3½ digits
Response Time	5 seconds
Warm-up time	Not required
Automatic Shut Off	2 minutes
Lamp	Tungsten Filament bulb (approximate life 800 hours)
Sample	15 mL in capped tube
Sample Chamber	Accepts 25mm diameter flat-bottomed tubes (capped)
Power source	Battery Operation: 9 Volt Alkaline Line Operation: 120V/50Hz, 220V/60Hz*, with supplied adapter
Size (L X W X H)	8.5 x 16.2 x 6.7 cm, 3.4 X 6.4 X 2.6 inches
Shipping Weight	Meter only: 11 oz. (312g) Kit: 3 lb. 7 oz. (1560g)
Serial Interface	RS232, 8 pin mDIN, 9600b, 8, 1, n

**CE Mark: The devise complies to the product specifications for the Low Voltage Directive when furnished with the 220V AC Adapter (Code 1774). The 120V AC adapter is not CE approved.*

PARTS & ACCESSORIES

Included in the Model 2020 Turbidity Meter Kit (Code 1799 OR 1799-EX2):

Code	*Item*
26856	2020 Turbidity Meter
1726-110	AC Adapter, 9V (or 1726-220 with 1799-EX2)
1476	AMCO™ 2020 Turbidity Standard, 1.0 NTU, 60 mL
1477	AMCO™ 2020 Turbidity Standard, 10 NTU, 60 mL
0286-4	Turbidity tubes, set of 4

Optional Accessories:

1478	AMCO™ 2020 Turbidity Standard, 100 NTU, 60 mL
1479	AMCO™ 2020 Turbidity Standard, 250 NTU, 60 mL
1800	High Turbidity Dilution Kit includes: Syringe, Filter Holder, Membrane Filters
0943	Syringe
0598	Filter holder
1103-6	Membrane Filters, 0.45 micron, pkg of 6
5115PS-H	Deionized Water, 60 mL
6195-H	Formazin Turbidity Standard, 4000 NTU, 60 mL

EPA COMPLIANCE

This instrument meets or exceeds EPA design specifications for NPDWR and NPDES turbidity monitoring programs as specified by the USEPA method 180.1. There is also a compliance reading mode which rounds the reading to meet EPA reporting requirements.

EPA COMPLIANT

WARRANTY

This instrument is guaranteed to be free from defects in material and workmanship for one year from original purchase date. If within that time the instrument is found to be defective, it will be repaired without charge except for transportation costs. The guarantee does not cover batteries.

one YEAR WARRANTY

CE COMPLIANCE

The 2020 Turbidimeter has been independently tested and has earned the European CE Mark of compliance for electromagnetic compatibility and safety.

DECLARATION OF CONFORMITY

Application of Council Directives:	89/336/EEC
Standards to which Conformity Declared:	EN55022, EN50082-1, En600950
Manufacturer's Name:	LaMotte Company
Manufacturer's Address:	802 Washington Avenue PO Box 329 Chestertown, MD 21620
Importer's Name:	Reagecon Diagnostics Ltd
Importer's Address:	13 A/D Shannon Free Zone Shannon, Co. Clase. Ireland
Type of Equipment:	Water Quality Meters
Model Number:	2020/1200
Year of Manufacture:	1997

I, the undersigned, hereby declare that the equipment specified above conforms to the above Directive and Standards.

Chestertown, Maryland
Place

James K. Trumbauer
Signature

3-19-97
Date

James K. Trumbauer
Name

V.P., Director of Research & Development
Position

NOTE: The device complies to the product specifications for the Low Voltage Directive when furnished with the 220V AC Adapter (Code 1774).

WHAT IS TURBIDITY?

Turbidity, cloudiness in water, can be interpreted as an absence of clarity or brilliance. It is caused by suspended and colloidal matter such as clay, silt, organic and inorganic matter and microscopic organisms. Turbidity should not be confused with color since a darkly colored water can still be clear and not turbid.

Turbid water is often an indicator of conditions that could cause damage to manufacturing equipment. Water clarity is especially important to the producers of consumer products such as beverage producers, food processors and water treatment plants. The particulates that cause turbidity may not always be harmful to human health, but are considered an undesirable characteristic.

Turbidity in industrial water used for boiler and cooling systems should be as low as possible. In boilers, the particles may become concentrated and settle out as a sludge that will damage equipment and cause foaming. In cooling water systems, particles can interfere with corrosion inhibitors. Water clarity is improved with fluid-particle separation processes such as sedimentation, coagulation and filtration.

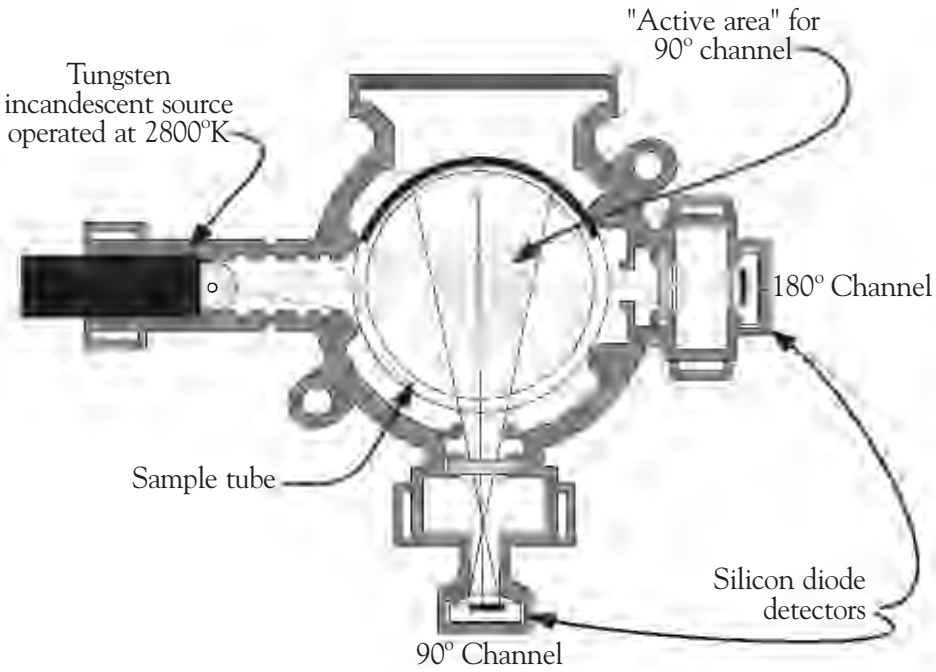
In swimming pools, cloudy water is a common problem. The usual causes for poor water clarity are corrosion, improper filtration and/or improperly balanced water. An algae condition or severe chloramine condition can also cloud pool water.

In natural waters, turbidity is an indicator of quality and productivity and can be used to monitor the health of streams and lakes. Turbid water may indicate runoff from construction, agriculture or other types of pollution. Suspended sediment can carry nutrients and pesticides throughout the water system. Suspended particles near the surface absorb additional heat from sunlight, raising the water temperature and blocking out the light needed by submerged aquatic vegetation and bottom dwelling creatures.

HOW IS TURBIDITY MEASURED?

Light passing through clear water will travel in a straight line. Particles in turbid water will cause the light to scatter giving it a "cloudy" appearance. The turbidity of a sample is determined by measuring the amount of scatter when a light is passed through a sample. The higher the turbidity, the greater the amount of scatter.

Turbidity can be measured in many ways. Visual methods include, the comparative methods, the Secchi disk method and the Jackson Candle method. Comparative methods are used in shallow water and determine turbidity by matching the turbidity of a water sample to a standard of known turbidity either with a "target" at the bottom of a tube or with a turbidity comparator. In the deeper waters of lakes, ponds, rivers and estuaries the Secchi disk is often used to measure turbidity. The Secchi disk is a disk about eight inches in diameter that is either white or is marked with black and white quadrants. The disk is lowered into the water on a calibrated line and the depth is noted where the disk just disappears from sight. The disk is then raised until it is visible. The average of these two distances is known as the "Secchi depth".



2020 Nephelometer

At waterworks and wastewater treatment plants the Jackson Candle apparatus was a standard instrument for measuring turbidities of incoming raw waters and treated wastewater effluents for many years. The equipment was modified over time but originally it consisted of a long glass tube supported over a "standard candle." Water was added to or removed from the tube until the image of the candle flame became indistinct. The depth of the water in the tube was read off a calibrated scale etched into the side of the tube, and results were reported numerically as Jackson Turbidity Units (JTU). The lowest turbidity that can be determined with this method is 25 Nephelometric Turbidity Units (NTU). Since the EPA's Surface Water Treatment requirements state that, finish water from municipal treatment plants will have a turbidity less than 1 NTU, indirect methods were developed to measure turbidity. Turbidimeters are the preferred method.

Nephelometers, such as the 2020, are turbidimeters that measure the scattered light at 90 degrees from the light source. A reference beam passes through the sample and is measured at 180 degrees. The ratio of these two readings is electronically converted to a turbidity measurement in NTU.

GENERAL OPERATING INFORMATION

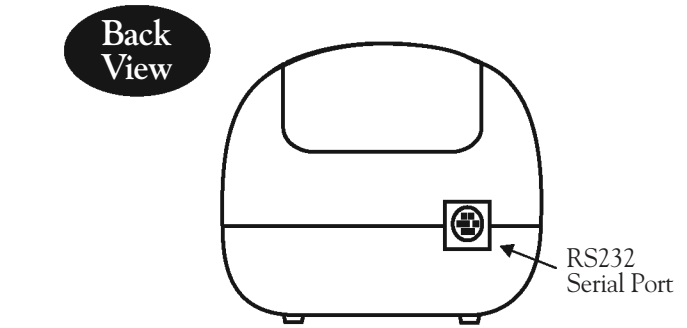
OVERVIEW

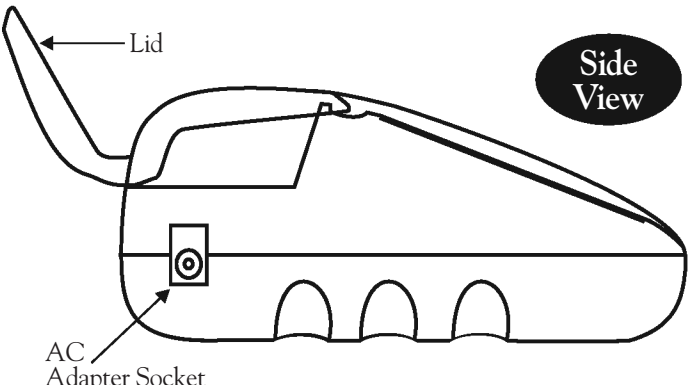
The 2020 Turbidimeter is a portable, microprocessor controlled nephelometer. A multi-detector optical configuration assures long term stability and minimizes stray light and color interferences. All readings are determined by the process of signal averaging over a 5 second period, minimizing fluctuations in readings attributed to large particles and enabling rapid, repeatable measurements. It has a sealed keypad. The microprocessor enables auto-ranging over the full range of 0 to 1100 NTU and provides direct digital readout with a resolution of 0.01 NTU for the lowest range.

The optics feature a tungsten bulb light source with a life expectancy of 800 hours. The light is detected by a silicon photo diode.

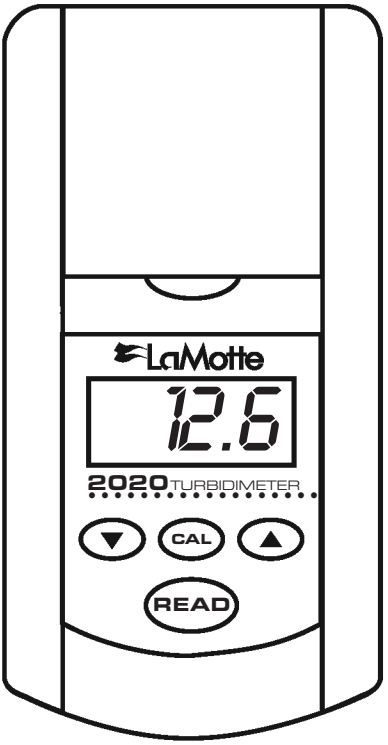
The 2020 is supplied with a 9 volt alkaline battery and an AC power adapter. A fresh battery should be installed at all times, even when using the power adapter. This will ensure that the meter will power down properly.

A RS-232 serial port on the back of the meter allows an interface of the turbidimeter with an IBM compatible computer for real time data acquisition and data storage using the PC. This port also allows an interface with a RS-232 serial printer.

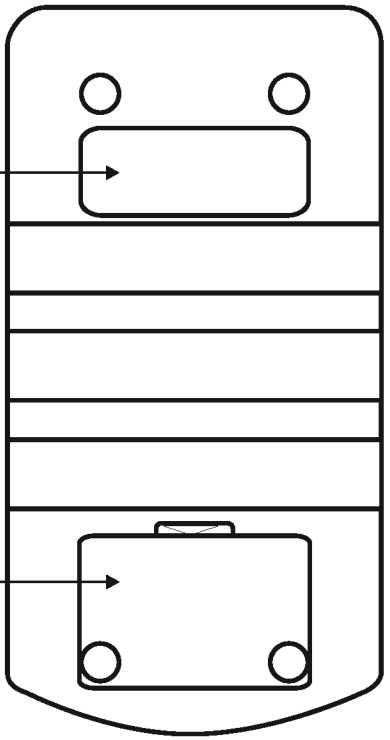




Top View



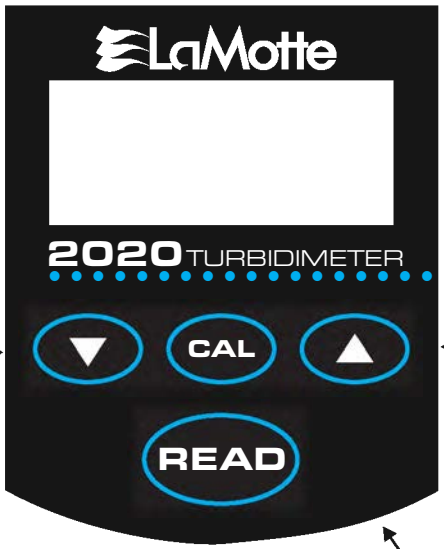
Bottom View



The DISPLAY will display turbidity reading with the following resolution:
0.00 - 10.99 NTU; 11.0 - 109.9 NTU; 110 - 1100 NTU

- When the **READ** button is first pushed, a number will be briefly displayed that indicates the software version number.
- A walking dash "-" will be displayed when measurement is taking place.
- The display will flash after the **CAL** button has been pushed during the calibration procedure until the **CAL** button has been pushed again to enter the adjusted value.
- "*OFF*" will be displayed after the **READ** button has been held down for 1 second. The meter will turn off when the button is released.
- "*ER1*" will be displayed when the battery voltage is very low.
- "*ER2*" will be displayed when measured turbidity is over range (1100 NTU).
- "*ER3*" will be displayed when the bulb has burned out or the tube is misaligned.
- "BAT" will be displayed when the battery voltage is getting low. Readings are reliable. Replace battery as soon as possible.
- "▲" will be displayed when the meter is in EPA mode.

See TROUBLE SHOOTING GUIDE page 23



The DOWN ARROW will **DECREASE** the numerical value of the display while in calibration mode.

The UP ARROW will **INCREASE** the numerical value of the display while in calibration mode.

The READ button is used to turn the meter ON and to take readings. Pressing the button for 1 second will cause the meter to display OFF. Releasing the button when OFF is displayed turns the meter OFF.

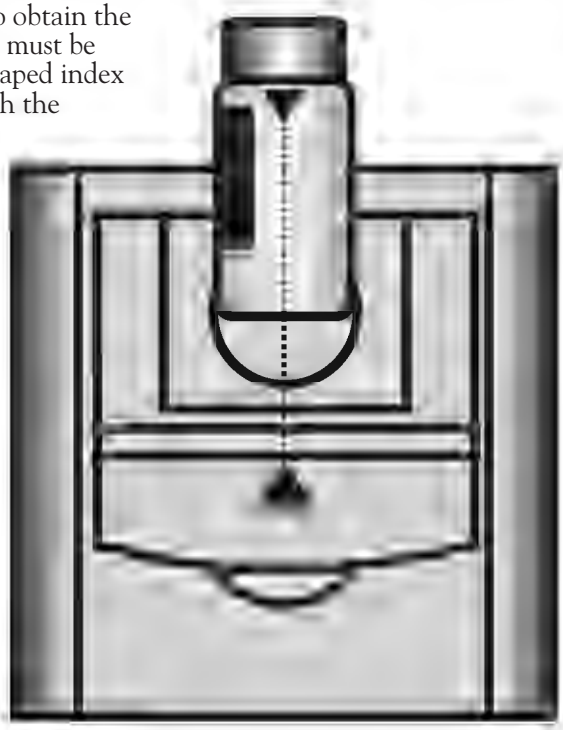
The CAL button is used for **CALIBRATION** procedures and to change between standard operating mode and EPA mode.

TURBIDITY TUBES

Turbidity tubes should always be washed prior to use. Use a mild detergent to remove any dirt or finger prints. Dry the outside of the turbidity tubes with a clean, lint-free cloth or disposable wipe. Allow the turbidity tubes to air-dry in an inverted position to prevent dust from entering the tube.

The handling of the turbidity tubes is of utmost importance. Scratches, fingerprints and water droplets on the turbidity tube or inside the light chamber can cause stray light interference leading to inaccurate results. It is imperative that the turbidity tubes and light chamber be clean and dry. Scratches and abrasions will permanently affect the accuracy of the readings. The inside of the tubes can be acid washed periodically and coated with special silicon oil to mask imperfections in the glass. Avoid acid contact with the black ink on the outside of the tubes. After a tube has been filled and capped, it should be held by the cap and the outside surface should be wiped with a clean, lint-free absorbent cloth until it is dry and smudge-free. Handling the tube only by the cap will avoid problems from fingerprints. Always set the clean tube aside on a clean surface that will not contaminate the tube.

Variability in the geometry and quality of the glassware is the predominate cause of variability in results. The special anti-reflective area on the 2020 tubes allows more accurate turbidity readings for low NTU samples. Only 2020 tubes should be used with the 2020 turbidimeter. Orientation of the tube in the chamber will greatly affect the test results. To obtain the most accurate results, the tubes must be positioned so that the arrow-shaped index mark on the tube is aligned with the arrow-shaped index mark molded into the housing in front of the light chamber. This will ensure that the most accurate results are obtained.

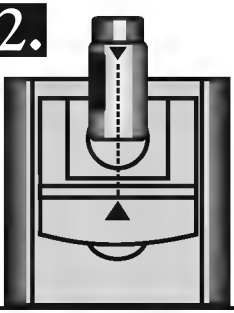


The 2020 turbidity tubes are optically selected but very small variations in the tubes may cause different readings on the same sample in low turbidity water. If greater accuracy is required, such as for Drinking Water requirements, the tubes supplied with the 2020 should be individually calibrated. This procedure is important for reading below 10 NTU but is probably not needed for samples above 10 NTU.

1.

Fill each tube (0286) with high-quality water. (Generally distilled water or drinking water is sufficient.)

2.



Record a turbidity reading for each tube following the instructions for turbidity measurement on page 19.

3.

Mark the tube with the lowest reading with an "R", for reference turbidity tube, near the top of the tube with a permanent marker.

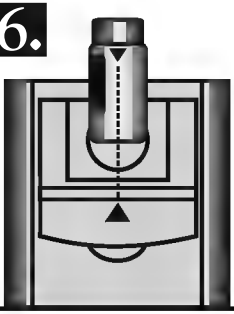
4.

Follow the Calibration Procedure on page 17 using the reference turbidity tube, turbidity-free water, and the 1.00 NTU or 10.0 NTU AMCO™ standard.

5.

Fill the remaining turbidity tubes with the same AMCO™ turbidity standard as in the reference turbidity tube.

6.



Insert each tube into the meter with the proper orientation, Close lid and record the reading for each tube.

7.

The difference between the theoretical value (1.00 NTU or 10.0 NTU) and the actual value is the correction factor for that tube. This factor should be used when comparing results from different tubes.

CALIBRATION

STANDARD SOLUTIONS

The 2020 has been pre-calibrated in the range of 0 to 1100 NTU with AMCO™ primary standards manufactured by Advanced Polymer Systems, Inc. This allows the 2020 to be used for treated water, natural water or wastewater. Recalibration of the 2020 by the user is not required. However, a procedure to standardize the calibration should be performed to obtain the most accurate readings over a narrow range.

Two AMCO™ standards of 1.00 NTU and 10.0 NTU are supplied with the 2020. Standards of other values are available as accessories. The standards are a suspension of uniformly sized plastic "micro spheres" in ultra pure water, which require no preparation and are stable for long periods of time. These standards were manufactured specifically as a reference to calibrate the 2020. Only LaMotte specific AMCO™ standards should be used with the 2020. These standards are guaranteed to be accurate to within ±1%, if the following precautions are observed:

- The standards will remain stable for up to 4 years prior to opening if stored between 10 and 40°C.
- Once the seal of the bottle is broken, the stability of the standard is only guaranteed for 1 year if stored between 10 and 40°C.
- Never pour any unused or used standard back into the primary standard bottle.
- Do not open the bottle in a dusty or dirty environment. Dust and contaminants from the air can ruin the quality of the standard solutions.
- Before filling a tube with a standard, rinse the inside of the tube with a small amount of standard.
- Cap the standard bottle and the tube immediately after filling.

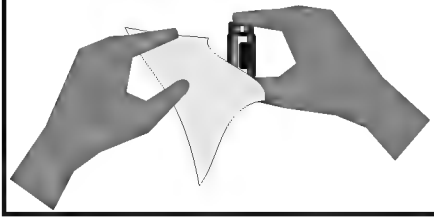
With proper preparation techniques, freshly prepared Formazin standards should be equivalent to the AMCO™ standards and can be used for meter calibration. A 4000 NTU Formazin Standard is available from LaMotte Company for use in preparing calibration standards. (See "Optional Accessories," pg. 6.) Correct procedures and approved methods for the use of Formazin standards can be found in the current edition of Standard Methods for Examination of Water and Wastewater.

CALIBRATION PROCEDURE

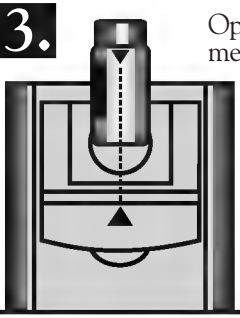
1.

Select a LaMotte AMCO™ 2020 Standard in the range of the samples to be tested. NOTE: Only use LaMotte AMCO™ Standards specific to the 2020 Turbidimeterr. Contact LaMotte for replacement standards.

2. Fill a turbidity tube with the standard, cap, and wipe the tube clean with a lint-free cloth.



3.



Open the lid of the meter. Align the indexing arrow mark on the tube with the indexing arrow mark on the meter, and insert the tube into the chamber.

4. Close the lid. Push the **READ** button. If the displayed value is not the same as the value of the reacted standard (within the specification limits), continue with the calibration procedure.

5.

Push the **CAL** button for 5 seconds until **CAL** is displayed. Release button. The display will flash. Adjust the display with the ▼ and ▲ buttons until the value of the standard is displayed.

6.

Push the **CAL** button again to memorize the calibration. The 2020 display will stop flashing. Calibration is complete.

7.

Turn the unit off by holding the **READ** button down for at least 1 second, or proceed to measure the test samples following the procedure on page 19.

Note

The calibration procedure should be followed once a week, or more often as required by regulations and laws for compliance monitoring. The calibration of the meter is independent of the operating mode.

ANALYSIS PROCEDURES

SELECTING THE EPA MODE

The 2020 turbidity meter has two operating modes, the standard operating mode and the EPA mode. The meter can only be switched from one mode to the other while turning the 2020 on, from the OFF state. The 2020 will remain in which ever mode it was last used, even if the meter has been turned OFF.

To switch from one mode to the other mode:

1.

Turn OFF the 2020, if it is on.

2.

Press **CAL** button and hold it down while pressing the **READ** button to turn the meter on.

The meter will come on in the opposite mode than it was in previously. (While in EPA mode the ▲ will be visible on the display).

The standard operating mode displays the measured turbidity to the full resolution of the meter. The EPA mode displays the measured turbidity rounded to the reporting requirements of the EPA and Standard Methods compliance monitoring programs. This greatly simplifies the reporting requirements by eliminating the need for the user to manually round off the results according to EPA specifications. The EPA requires these reporting requirements because it recognizes the inherent accuracy of turbidity measurements within the specified ranges.

Note: The calibration of the meter is independent of the operating mode.

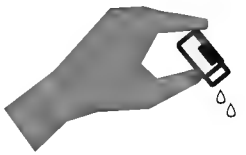
TURBIDITY MEASUREMENT

1.

Fill a clean container with at least 50 mL of sample water and cover. Set sample aside to allow sample to equilibrate to air temperature and let gases escape. Avoid contaminants. Analyze as soon as possible.

2.

Rinse an empty turbidity tube with a portion of the sample. Shake out excess water.

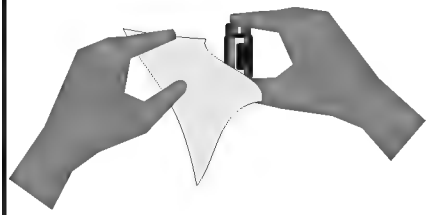


3.

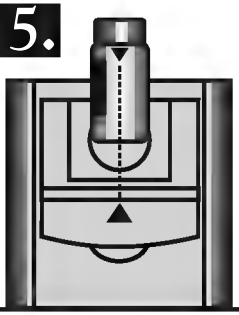
Fill the turbidity tube (0286) to the neck by carefully pouring the sample down the side of the tube to avoid creating bubbles.

4.

Cap the tube and wipe tube dry with a clean lint-free tissue.



5.



Open the 2020 lid. Align the indexing arrow on the tube with the indexing arrow on the meter. Insert the turbidity tube into chamber.

6.

Close the lid. Push the **READ** button. The turbidity in NTU units will be displayed within 5 seconds.

7.

The 2020 will turn off automatically 2 minutes after the last button push. To turn the meter OFF manually, hold the **READ** button down for at least 1 second. Release the button when OFF is displayed.

Note

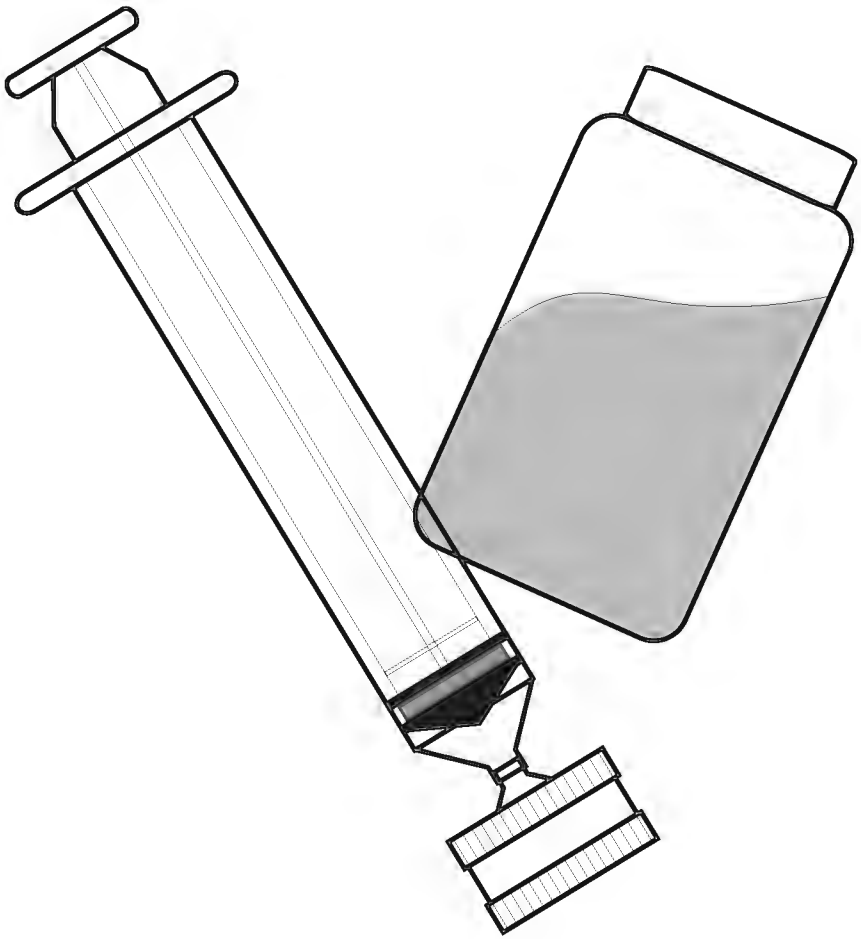
If the sample is higher than 1100 NTU, it must be diluted and retested. See pages 20-22.

PREPARATION OF TURBIDITY FREE WATER

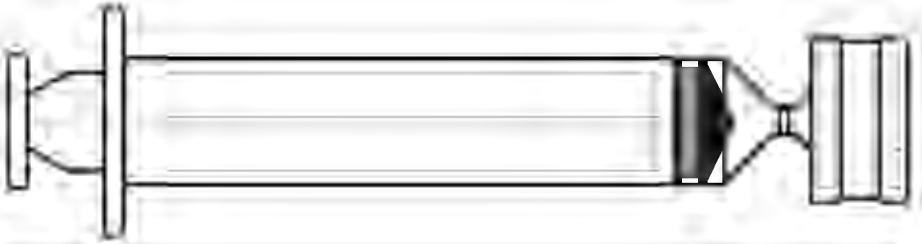
An accessory package (Code 1800, not included) is available for preparing turbidity free water for dilution of high turbidity samples.

The preparation of turbidity free water requires careful technique. Introduction of any foreign matter will affect the turbidity reading. A filtering device with a special membrane filter is used to prepare turbidity-free water. The filter, filter holder, and syringe must be conditioned by forcing at least two syringes full of deionized water through the filtering apparatus to remove foreign matter. The first and second rinses should be discarded. Turbidity-free water as prepared below may be stored in the dark at room temperature in a clean glass bottle with a screw cap and used as required. The storage container should be rinsed thoroughly with filtered deionized water before filling. The water should be periodically inspected for foreign matter in bright light.

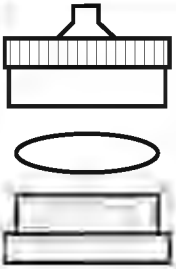
See procedure on next page…



PROCEDURE:



1.

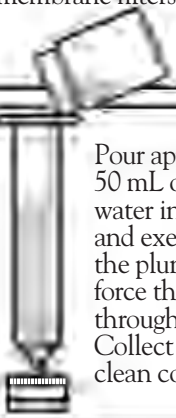


Unscrew the top of the filter holder (0598). (The black O-Ring should remain in the top part of the filter holder). Place a white membrane filter (1103) on the screen inside. Position the filter disk so that it covers the entire surface of the screen. Replace the top of the filter holder and screw on securely. Note: the membrane filters are white and packaged between two blue protective disks. Handle membrane filters with extreme care.

2.

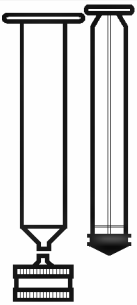
Remove the plunger from the syringe (0943). Attach filter holder to the bottom of the syringe.

3.



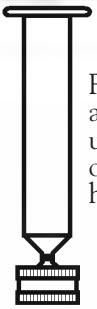
Pour approximately 50 mL of deionized water into the barrel and exert pressure on the plunger to slowly force the water through the filter. Collect water in a clean container.

4.



Remove the filter holder from the syringe, then remove the plunger from the barrel. (This step is required to prevent rupturing the membrane filter by the vacuum as the plunger is removed.)

5.



Replace the filter holder and repeat steps 3 and 4 until the desired amount of turbidity-free water has been collected.

Periodically examine the membrane filter to insure that no holes or cracks are present. Depending on the nature of the unfiltered water, it is possible to prepare a liter or more of turbidity-free water using a single filter. The membrane filter may be stored in the holder indefinitely and used as required.

DILUTION PROCEDURES

If a sample is encountered that is higher than 1100 NTU, a careful dilution will bring the sample into the acceptable range. However, there is no guarantee that halving the concentration will exactly halve the NTU values. The particulates often react in an unpredictable manner when diluted.

TESTING TIPS

1. Samples should be collected in a clean glass or polyethylene container.
2. Samples should be analyzed as soon as possible after collection.
3. Discard tubes that are badly scratched.
4. Gently mix sample by inverting before taking a reading but avoid introducing air bubbles.
5. Turbidity readings will be affected by electric fields around motors.
6. Carbon in the sample will absorb light and cause low readings.
7. Observe shelf life recommendations for turbidity standards.
8. The turbidimeter should be placed on a surface free from vibration. Vibrations can cause high readings.
9. Excessive color in a sample will absorb light and cause high readings. The user should verify if a certain level of color will cause a significant error at the level of turbidity being tested.

TROUBLESHOOTING

PROBLEM	CHECK	ACTION
No Power	Battery	Replace
	AC Adapter	Plug in
	AC Wall Outlet	Verify power source
	Contact LaMotte for Return Authorization	Return to LaMotte for repair
Suspect Calibration	Check calibration with standards	Use new standards
	Verify standards with Formazin	Run alternate test with Formazin
	Verify with another meter	Check other meter calibrations
	Check tube alignment	Re-align tube
	Check sample tubes for dirt and scratches	Check, clean and/or replace if necessary
	Check to see if internal meter components are wet	Always dry tubes before inserting. Examine chamber for visible moisture.
	Reset meter to factory calibration	With meter off, hold down ▼ and press **READ**
	Battery	A fresh battery should be installed at all times, even when using the power adapter. This will ensure that the meter will power down properly and the calibration will not be lost. Return meter for recalibration.
	Contact LaMotte for Return Authorization	Return for calibration check
ER1	Very low battery	Change battery
ER2	Over range	Dilute sample
ER3	Burnt out bulb or misaligned tube	Check alignment Call LaMotte
BAT	Low Battery	Change battery

RS232 PORT

The 2020 Turbidimeter may be interfaced with any IBM compatible computer using an Interface cable (Code 1772). The meter may also be interfaced with an RS-232 serial printer, using an appropriate cable and setting the printer configuration to the output below.

Output: RS232 compatible, asynchronous serial, 9600 baud, no parity, 8 data bits, 1 stop bit.

Computer Connection: RS232 interface connection, 8 pin mDIN/9 pin F D-submin.

Pin out:

5	RS-232 TxD
3	RS-232 RxD
4, 6, 8	digital ground

MAINTENANCE

REPLACING THE BATTERY

The LaMotte 2020 uses a standard 9-volt alkaline battery that is available worldwide. A fresh battery should be installed at all times, even when using the power adapter. This will ensure that the meter will power down properly. The battery compartment is located on the bottom of the case. To replace the battery:

1. Open the battery compartment lid
2. Remove the battery and disconnect the battery from the polarized plug.
3. Carefully connect the new battery to the polarized plug and insert it into the compartment.
4. Close the battery compartment lid

REPLACING THE LAMP

The tungsten lamp included with the model 2020 has a life of approximately 800 hours. If the display becomes unstable when using LaMotte AMCO™ standards, call LaMotte Company for a return authorization number to have the lamp replaced and have the unit examined.

REPAIRS

If it is necessary to return the instrument for repair, telephone LaMotte Company at 1-800-344-3100 or fax 1-410-778-6394 for a return authorization number.

LaMOTTE COMPANY

Helping People Solve Analytical Challenges®

PO Box 329 • Chestertown • Maryland • 21620 • USA
800-344-3100 • 410-778-3100 (Outside U.S.A.) • Fax 410-778-6394
Visit us on the web at www.lamotte.com

10/02 • 61799

Using the MiniRAE 2000 & ppbRAE PID

Firmware v. 1.20 (rev C)

The Hazardous Environment Detection Company

RAE SYSTEMS

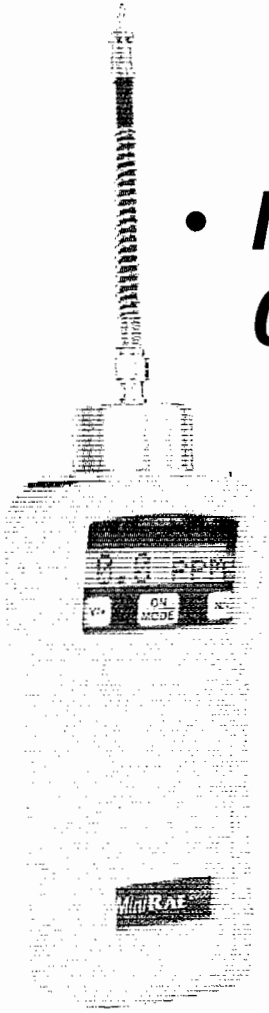
Training Agenda:

- MiniRAE 2000 & ppbRAE features
- Turning on the MiniRAE 2000 & ppbRAE
- Recommended Daily Start-up Procedure
- User modes & displays
- Alarm modes
- Programming displays
- Calibration

The Hazardous Environment Detection Company

RAE SYSTEMS

MiniRAE 2000/ppbRAE



- ***MiniRAE 2000: 0.1-10,000 ppm***

- ***pppRAE: 1-9999 ppb/ 0.1-2000 ppm***

The Hazardous Environment Detection Company

RAE SYSTEMS

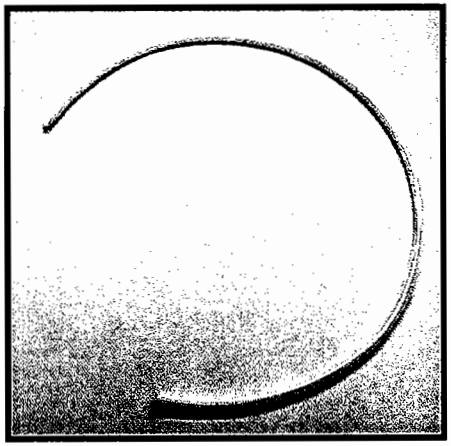
RAE 2000: Internal Pump

- 500 cc/min makes remote sampling easy
- Sample draw over 100 feet!
- Use external white liquid water trap for added protection
- Pump stall feature: when moisture is detected or when pump is blocked the pump will shut off, protecting the MiniRAE 2000 from potential damage
- Runs 10 hours with pump
- Only use Teflon tubing

The Hazardous Environment Detection Company

RAE SYSTEMS

MiniRAE 2000: Tubing



- Never Use Tygon tubing!
  - Absorbs chemicals like a "sponge"
  - Reduces ppm readout when chemicals exist
  - Causes "false positives" when chemicals don't exist
- Always use Teflon or similar non-reactive tubing
  - Will not absorb chemicals but might get coated
  - Clean with anhydrous methanol if it gets dirty

The Hazardous Environment Detection Company

RAE SYSTEMS

E 2000: External Prefilter

- Use the white external prefilter in high moisture environments like rain and saturated headspace sampling.
- Replace filter when it looks very dirty or when it introduces PID drift.
- Replace filter when in pump alarm with the filter on and you can clear the pump alarm with the filter off.
- Consider eliminating external prefilter & internal C-filter when measuring high-boiling/flashpoint chemicals (phenols, CWA)

The Hazardous Environment Detection Company

RAE SYSTEMS

MiniRAE 2000: Reliability

- Extremely rugged for extensive field use
- Weather Proof Case with gasketed case breaks
- Temperature range of 14°F to 113°F (-10°C to 40°C)
- 4-Way power: NiMH, Alkaline or run continuously on 110 VAC and 12 VDC
- RFI protection against radio interference
- Intrinsically safe: Class I, Division I, Groups A, B, C, D

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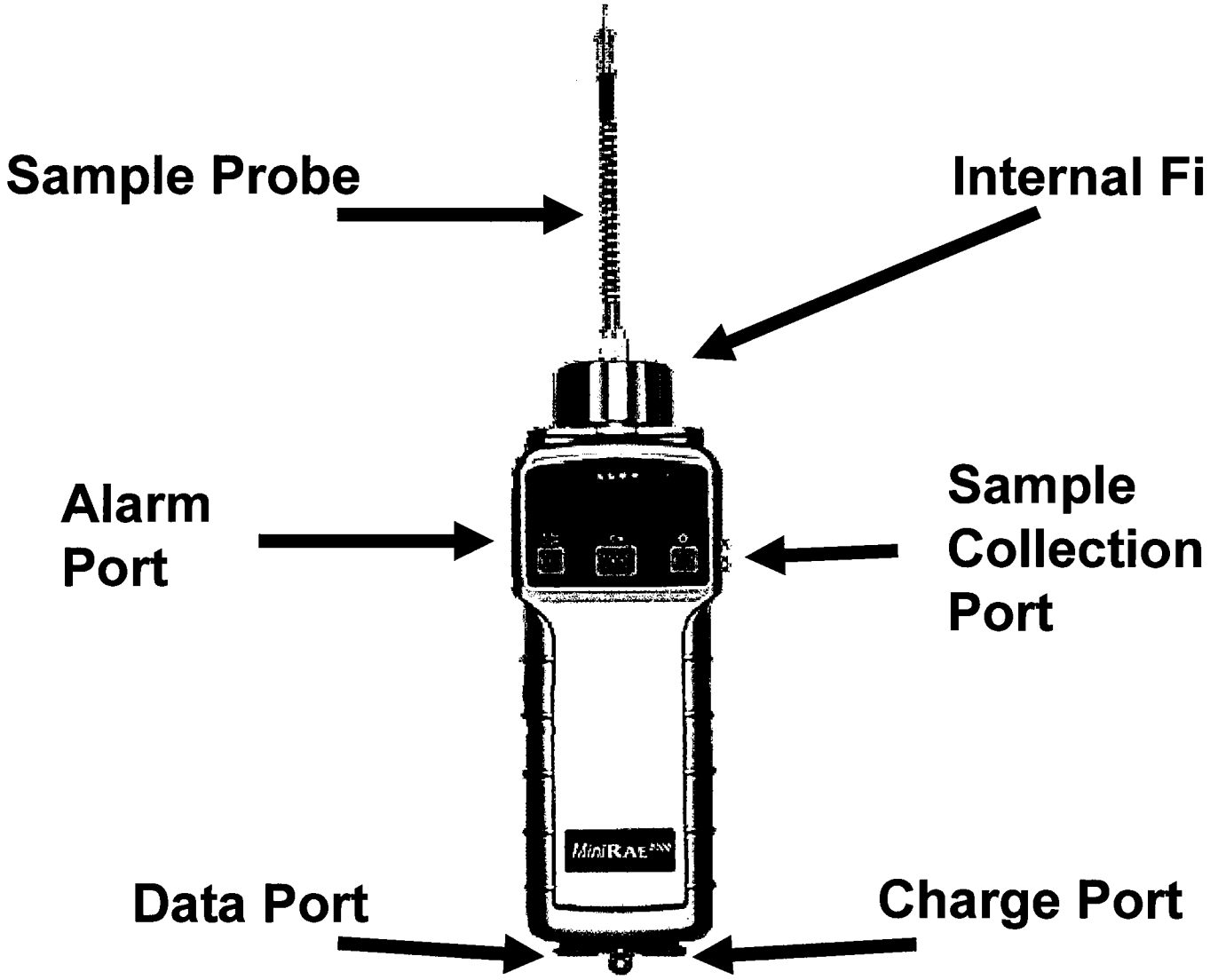
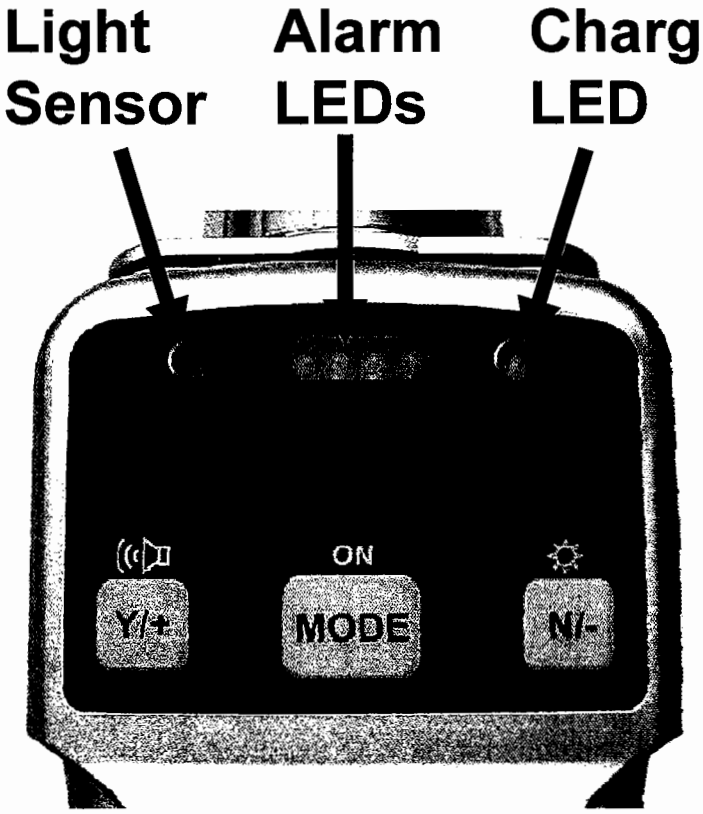
RAE SYSTEMS

AE 2000: Physical Description



MiniRAE 2000: Faceplate

- Three buttons on a sealed membrane faceplate:
  - Y/+ (horn): clears & tests alarms
  - N/- (light): turns on manual backlight for 60 seconds
  - MODE (on)



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RAE SYSTEMS

Start-up: Turning On

- Unplug MiniRAE 2000/ppbRAE from charger
- Hold “MODE” Key to turn on
- Alarm will beep once
- Watch display screen for configuration messages.
- Warm-up will take approximately 30 seconds

RAE SYSTEMS

2000: Survey/Hygiene Mode

The MiniRAE 2000 and ppbRAE have two main operating modes:

- **Survey Mode:** the factory default mode. After warm-up the pump shuts off and "Ready" is displayed.
- **Hygiene Mode:** for health and safety applications. After warm-up the meter samples continuously (similar to MultiRAE & AreaRAE).

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RAE SYSTEMS

iRAE 2000: Survey Mode

- A discrete sampling mode can easily start/stop datalogging for many points
- Perfect for drum or headspace sampling

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RAE SYSTEMS

Survey Displays

Ready/Instantaneous reading

Stop?

Avg: shows average reading

Peak: holds highest reading

Run Time:

Battery Voltage & Shut-Off

Date/Time/Temperature: (MiniRAE 2000 Only)

Log On/Off? Starts Manual Datalog

Cancel/Show Background: ppbRAE only

PC comm?

Advance to next screen with "Mode" key

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RAE SYSTEMS

rvey Mode: Ready Screen

Ready...

- After warm-up the pump will stop and display will read “Ready...” The MiniRAE is in stand-by mode ready for sampling.
- To start sampling push the “Y” key

Site ID = Drum 043

- The Site ID screen will increase by one digit every time that the MiniRAE is started and stopped in Survey Mode.

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RAE SYSTEMS

Survey Mode: Ready Screen

Gas = Isobutylene

- The "Gas =" screen shows the Correction Factor (CF) Gas currently in use.
- Stop sampling in survey mode by pressing the mode key. The display will show "Stop ?"

Stop ?

- Pressing "Y" will stop sampling and return to the "Ready" screen.

RAE SYSTEMS

Start-up: Lamp Alarm

0.0 Lamp

"Lamp" display along with audible alarm indicates that PID lamp has failed to light

If after a few minutes the "Lamp" message remains, turn off MiniRAE 2000 and restart

If after restart "Lamp" message disappears, MiniRAE 2000 is ready for use

If after restart "Lamp" message remains, the PID needs service

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RAE SYSTEMS

Start-up: Pump Check

0.0 Pump

Every time the MiniRAE 2000 is used it is important to check pump flow

Block the probe inlet, the MiniRAE 2000 will go into alarm and display “Pump”

Reset pump alarm by pressing the “Y” key

If pump does not go into alarm, check for leaks in the probe or service pump

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RAE SYSTEMS

Survey Mode: Alarms

50.0 ppm

The MiniRAE 2000 will beep twice per second when the low alarm has been exceeded.

The MiniRAE 2000 will beep three times per second when the low alarm has been exceeded.

Press “Y/+” key to clear if latching alarm.

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RAE SYSTEMS

rvey Mode: Peak Clearing

Peak 78.0 ppm

Press the "Y" key once during the "Peak" display

Reset Peak?

Pressing the "Y" key once during the "Reset Peak?" screen will clear the Peak Hold feature

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RAE SYSTEMS

giene Mode: Datalog Indicator

0.0 L ppm

- The small "L" indicates that the MiniRAE 2000 is datalogging.

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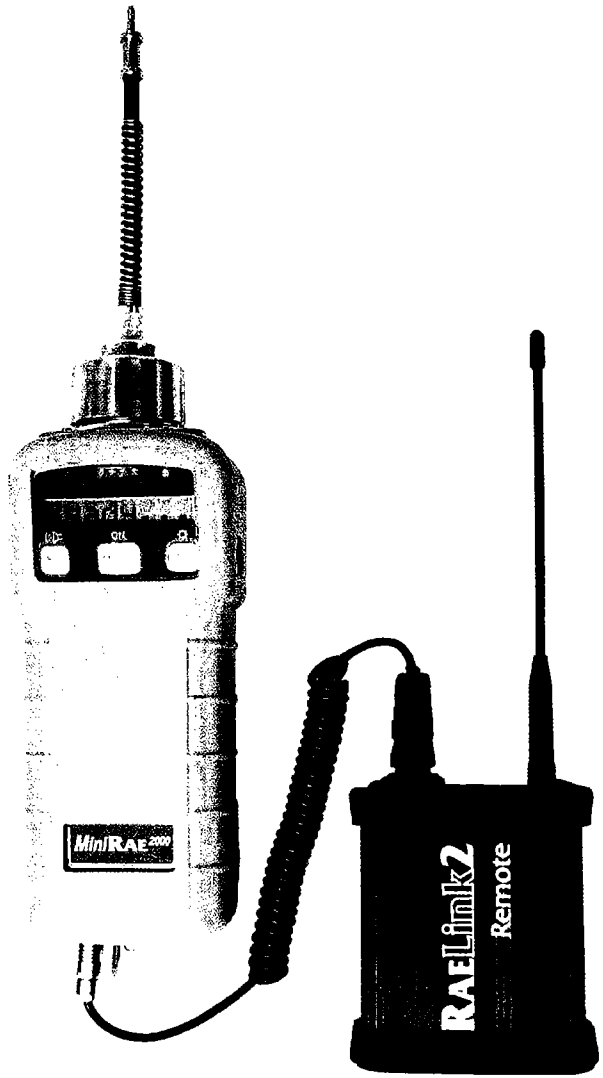
RAE SYSTEMS

lene Mode: Wireless Indicator



0.0 T ppm

- The small "T" indicates that the MiniRAE 2000 or ppbRAE is communicating to a host computer running ProRAE Remote software via the optional wireless RAELink modem.

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RAE SYSTEMS

RAE: Canceled Background

0.0 + ppm

- The ppbRAE has the ability to cancel the background without recalibration.
- When background is canceled, alarms are still based upon actual levels. Datalogging records actual levels.
- The small "+" indicates that the background has been canceled.

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RAE 2000: Hygiene Mode

- A continuous sampling mode for health & safety applications like confined space entry.
- Alarms are just like those on the MultiRAE, QRAE and ToxiRAE

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RAE SYSTEMS

Hygiene Displays

Instantaneous reading

TWA: *Time Weighted Average*

STEL: *Short Term Exposure Limit (displays "****" unit 15 minutes of run time have elapsed)*

Peak: *holds highest reading*

Run Time

Battery Voltage

Advance to next screen with "Mode" key

Date/Time/Temperature: *(MiniRAE 2000 only)*

Log On/Off? *Starts Manual Datalog*

Cancel/Show Background: *(ppbRAE only)*

Gas= *Correction Factor Gas (MiniRAE 2000 only)*

PC comm?

The Hazardous Environment Detection Company

RAE SYSTEMS

ygiene Mode: High Alarm

9999 High

"High" display along with 3 beep audible alarm, flashing alarm LEDs and flashing display backlight indicates that the High alarm setpoint has been exceeded.

Press "Y/+" key to clear if latching alarm.

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RAE SYSTEMS

Hygiene Mode: Low Alarm

50.0 Low

"Low" display along with 2 beep audible alarm, flashing alarm LEDs and flashing display backlight indicates that the Low alarm setpoint has been exceeded.

Press "Y/+" key to clear if latching alarm.

The Hazardous Environment Detection Company

RAE SYSTEMS

ygiene Mode: STEL Alarm

50.0 STEL

"STEL" display along with 1 beep per second audible alarm, flashing alarm LEDs and flashing display backlight indicates that the Short Term Exposure alarm setpoint has been exceeded.

This alarm will only clear if the average concentration dips below the STEL alarm setpoint or the PID is turned off.

The Hazardous Environment Detection Company

RAE SYSTEMS

ygiene Mode: TWA Alarm

50.0 TWA

"TWA" display along with 1 beep per second audible alarm, flashing alarm LEDs and flashing display backlight indicates that the Time Weighted Average alarm setpoint has been exceeded.

This alarm will only clear if the average concentration dips below the TWA alarm setpoint or the PID is turned off.

The Hazardous Environment Detection Company

RAE SYSTEMS

Y/Hygiene Mode: Pump Alarm

0.0 Pump

"Pump" display along with 3 beep audible alarm indicates that pump has stopped due to line clog or a clogged sample port.

Pump alarm is a latching alarm

Press "Y/+" key to clear alarm and restart pump

The Hazardous Environment Detection Company

RAE SYSTEMS

Hygiene Mode: Battery Alarm

0.0 Bat

A flashing "Bat" display along with a 1 beep alarm every 10 seconds indicates that the battery voltage is low and MiniRAE 2000 or ppbRAE will shut down in 20-30 minutes

Full battery is over 4.8 volts

Low Bat alarm at 4.4 volts

Shut down at 4.2 volts

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RAE SYSTEMS

Getting Into Programming

- *Hold "MODE" and "N/-" keys for 5 sec. to get in Programming Mode*
- If MiniRAE 2000 asks a question "?"
  - Answer "Y" or "N"
- To Accept or Escape
  - Use "MODE" Key
  - repeatedly pushing the "MODE" key will always eventually return user to main display

RAE SYSTEMS

Programming Menus

- Calibrate/select Gas? *(alarms are silenced when in this menu)*
- Change alarm limits?
- View/change datalog?
- Change monitor setup?
- *Choose (Y) to accept or (N) to move on*

If you get lost, refer to Appendix A-1 in MiniRAE 2000 Manual

RAE SYSTEMS

Calibrate Monitor?

- Fresh air/Zero cal?
  - *Make sure air is clean or use Charcoal filter*

  - *From v1.20 on, ppbRAEs do not use an electronic zero, so make sure to use a VOC Zeroing tube or Ultra-zero air*
  - *Refer to TN-150 for ppbRAE zeroing*
- Span cal?

Choose (Y) to accept or (N) to move on, MODE to escape

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RAE SYSTEMS

Basic Span Calibration

Cal gas = Isobutylene

Span value = 0100.0

These two screens MUST match the type and concentration of cal gas used (MiniRAE is ppm, ppbRAE in ppb)

If they do not, reset the MiniRAE to "Cal Memory 0" under the "Select Cal Memory" menu.

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RAE SYSTEMS

Basic Span Calibration

Apply gas now!

Attach calibration hose to MiniRAE 2000 and make sure it is tight

Turn on calibration gas and it will be automatically detected by the MiniRAE

Follow instructions on screen

Disconnect regulator when finished calibration

RAE SYSTEMS

Basic Span Calibration

NO Gas!

If you get this screen check for gas flow

Try span calibration again after you have verified that the gas is correct and is flowing properly through the regulator

Press [Y/+] if gas is OK to override the message and start the calibration

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RAE SYSTEMS

Matched Flow Calibration

For best accuracy a matched flow calibration is required!

- Use matched flow regulator
- Fill Tedlar bag with calibration gas and then draw down with MiniRAE 2000
- Use "T" or open tube connection with excess flow

ppbRAE always requires matched flow calibration!

RAE SYSTEMS

Calibrate Monitor?

- Select cal memory?
  - *For most uses, leave on "Cal Memory 0", which is for Isobutylene calibration and optional correction factors*
  - *Changing the cal memory lets you calibrate using a gas other than Isobutylene*
  - *Lets you load 7 frequently used gases*
  - ***For advanced users only***

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RAE SYSTEMS

Calibrate Monitor?

- Change span value? (*NOTE: the value in the ppbRAE is in parts per billion not ppm! 10000 ppb = 10 ppm)*
- Modify cal memory?
  - *Changes Measurement Gas name, Correction Factor* ***AND ALARM POINT***
- Change correction factor?

Choose (Y) to accept or (N) to move on, MODE to escape

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RAE SYSTEMS

Change Alarm Limits?

- High limit?
- Low limit?
- STEL limit?
- TWA limit?
  - *These values are set to the default values for each gas selected under "Modify Cal Memory" but can be modified in these menus.*

Choose (Y) to accept or (N) to move on, MODE to escape

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RAE SYSTEMS

View/Change Datalog?

- Reset Peak? (not in ppbRAE)
- View data?
- Clear data?
- Change data period?
- Change average type?

Choose (Y) to accept or (N) to move on, MODE to escape

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RAE SYSTEMS

Change Monitor Setup?

- Change Op Mode? *Survey or Hygiene*
- Change Site ID?
- Change User ID?
- Change Alarm Mode? *Reset or Latched*
- Change User Mode? *Program/Display*
- Change Date?
- Change Time?

Choose (Y) to accept or (N) to move on, MODE to escape

RAE SYSTEMS

Change Monitor Setup?

- Change Lamp? *(9.8, 10.6, 11.7 eV)*
  - *ppbRAE 10.6 eV only*
- Change Lamp Duty Cycle?
  - For self-cleaning during continuous operation
  - Pump runs then turns off, the lamp remains on to clean the sensor and lamp surface
  - When concentration exceeds 2 ppm the pump runs continuously until the concentration drops
  - Set to 30-100%. Time on in a 10 second interval. If set to 30% then on 3 seconds off 7 seconds. If set to 50% then on 5 off 5 seconds.
  - Will reduce loss of span sensitivity to <5% running 24/7 for over 90 days in backgrounds of <10 ppm (Refer to TN-165)

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RAE SYSTEMS

Change Monitor Setup?

- Change Unit? *(ppm or mg/m3)*
- Change Pump Speed? (ppbRAE only)
- Change Dilution Ratio? (M2K only)
- Change Output? *(DAC or Alarm)*
- Change DAC range? *(20, 200, 2000, 10k ppm)*
- Set Temperature Unit? (°C or °F)

Choose (Y) to accept or (N) to move on, MODE to escape

The Hazardous Environment Detection Company

RAE SYSTEMS

Power Off

- Hold Mode Key for full 5 seconds
- Audible alarm will beep and display will read “Power-down in ...5 seconds”
- Leave MiniRAE 2000 on charger when not in use

Deep Discharge?

- Plug 12 VDC charger into charge port
- The screen will display "Deep Discharge?" for 10 sec.
  - ***Pushing "N/-" will initiate charging***
  - ***Don't push anything and the unit will switch to charge in 10 sec.***
  - ***Full charge can take up to 8 hours***
  - ***Deep Discharge is not necessary for Nickel Metal Hydride batteries in MiniRAE 2000 or ppbRAE***

The Hazardous Environment Detection Company

RAE SYSTEMS

ppbRAE 2000: Self-Cleaning

Patented RAE Systems Breakthrough!

- Lamp runs for 4 hours during charging
- Generates small amounts of ozone which helps to scrub sensor and lamp clean
- With probe removed user will see the sensor glow purple during charging
- Does not decrease lamp life
- Drastically increases PID stability and reduces requirement for cleaning (Refer to TN-165)

RAE SYSTEMS

Maintenance

- Clean PID Lamp & Sensor
  - When display creeps upwards after good zero
  - When PID responds to moisture
  - When movement of PID results in response on display

Clean Sensor

No dirt build-up to foster a decrease in airspace resistance

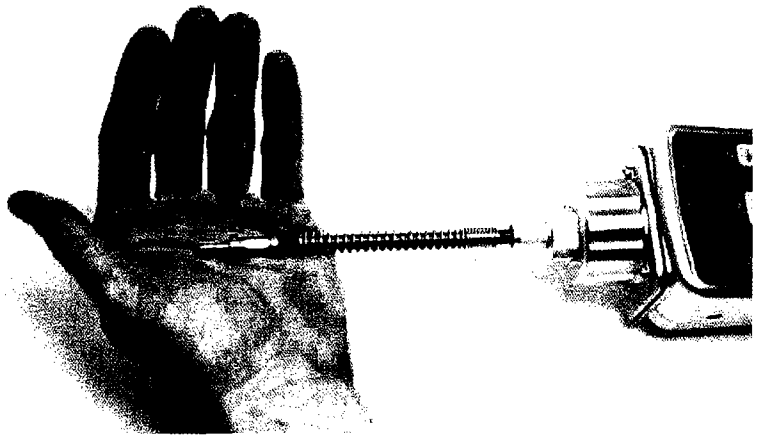
Dirty Sensor

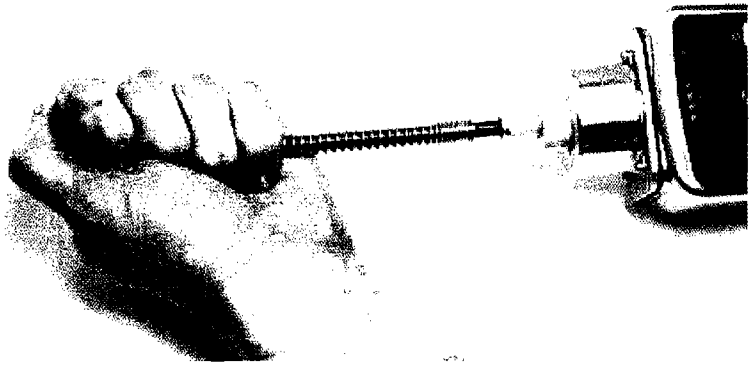
Dirt build-up absorbs water and breaks down airspace resistance leading to sensor "leakage" or moisture response

RAE SYSTEMS

Maintenance

- Humidity Check
  - Cup hand over inlet or breathe into inlet for 10-20 seconds
  - Do not block flow
  - If M2K reads >2 ppm or ppbRAE reads >500 ppb, then the sensor needs cleaning





RAE SYSTEMS

Maintenance

- How to Clean PID Sensor
  - Always clean sample probe and replace or clean filters FIRST! If PID holds a stable zero after this step then further cleaning may not be necessary
  - Use anhydrous methanol (Lamp cleaning solution)
  - Clean lamp face with lens tissue
  - Clean sensor by immersion in cleaning solution
  - Ultrasonic Cleaner (Jewelry cleaner) for 15 min. cleans much better than just dipping in
- Drying the PID Sensor
  - Let air dry overnight
  - Warm air (not hot) will speed drying

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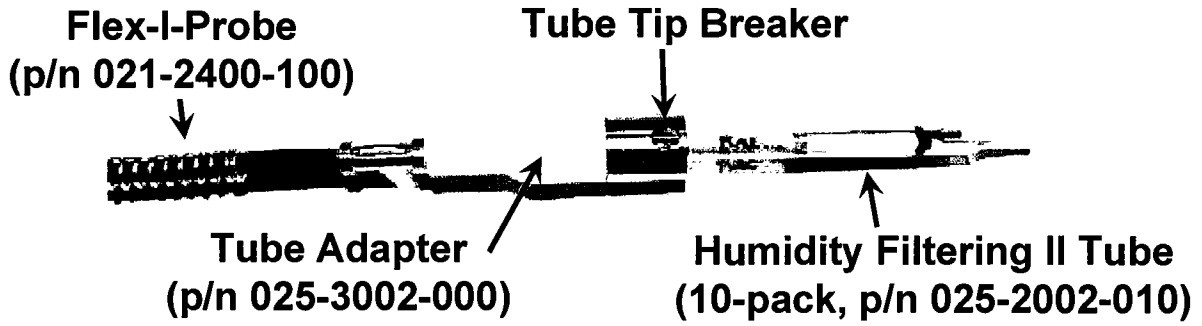
RAE SYSTEMS

Humidity Filtering II Tubes



- Temporary relief for a dirty sensor
- Dries sample gas for about ½ hour
- Measure VOCs; multiple sample use OK
- Useful for gasoline and chlorinated solvents
- **CAUTION:** May cause low response for some compounds or at low temperature or concentration

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RAE SYSTEMS

Configuration from Computer Datalogging

The Hazardous Environment Detection Company

RAE SYSTEMS

Questions?

Service: 888-723-4800

Sales: 877-723-2878

Tisch Environmental, Inc.

OPERATIONS MANUAL

TE-6000 Series
TE-6070, TE-6070-BL, TE-6070D, TE-6070D-BL
TE-6070V, TE-6070V-BL, TE-6070DV, TE-6070DV-BL

PM10

Particulate Matter 10 Microns and less
High Volume Air Sampler

U.S. EPA Federal Reference Number
RFPS-0202-141

145 South Miami Avenue
Village of Cleves, Ohio 45002

Toll Free: TSP AND - PM10
(877) 263 - 7610
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FAX: (513) 467-9009
Web Site: www.Tisch-Env.com
Email: sales@tisch-env.com

PREFACE: Information within this Operation Manual has been compiled from many users and drawn from many years of experience. More detailed information about PM-10 sampling is available from the United States Environmental Protection Agency. The EPA has published a Quality Assurance Handbook Section 2.11, which can be used for supplemental guidance. Additional information can be found in 40 Code of Federal Regulations Part 50, Appendixes J and M. Appendix J is printed within this document. An additional on-line source of information is available at **www.epa.gov/ttn/amtic**.

Tisch Environmental, Inc. produces a broad range of pollution measuring instruments for all types of industrial, service and governmental applications. TEI is a family business located in the Village of Cleves, Ohio. TEI employees skilled personnel who average over 20 years of experience each in the design, manufacture, and support of air pollution monitoring equipment. Our modern well-equipped factory, quality philosophy and experience have made TEI the supplier of choice air pollution monitoring equipment. Now working on the fourth generation, TEI has state-of-the-art manufacturing capability and is looking into the future needs of today's environmental professionals.

CONTENTS **Page**

Warranty

Tisch Environmental, Inc. warrants instruments of its manufacture to be free of defect in material and workmanship for one year from the date of shipment to the purchaser. Its liability is limited to the service or replacing any defective part of any instrument returned to the factory by the original purchaser. All service traceable to defects in original material or workmanship is considered warranty service and is performed free of charge. The expense of warranty shipping charges to and from our factory will be borne by Tisch Environmental. Service performed to rectify an instrument malfunction caused by abuse or neglect and service performed after the one year warranty period will be charged to the customer at the then current prices for labor, parts, and transportation. The right is reserved to make changes in construction, design, and prices without prior notice.

Quality Policy

Tisch Environmental, Inc. specializes in the manufacture and supply of quality, reliable and safe equipment for environmental studies.

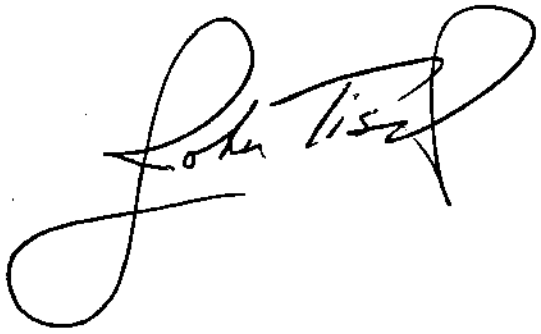
The objective of the company is to supply products that are fit for use and have the desired quality in accordance with customer requirements and published specifications. Our customers expect safe, reliable and optimum cost products delivered on time.

To achieve the above objective and satisfy the customer expectations, the Company is totally committed to implementing and maintaining the Quality Management System based on ISO9002.

Quality problems arising in various areas are to be identified and solved with speed, technical efficiency and economy. We shall focus our resources, both technical and human, towards the prevention of quality deficiencies to satisfy the organizational goals of “right first time…every time”.

The successful operation of the system relies upon the co-operation and involvement of personnel at all levels. Our commitment to quality will ensure the continued success of our Company and the satisfaction of our customers and staff.

The Quality Coordinator is authorized to ensure that the requirements of this Quality System are implemented. Any problems that can not be solved between departments or personnel shall be brought to my attention for final resolution.



President

Tisch Environmental, Inc.

WARNINGS OF SAFETY HAZARDS/SAFETY PRECAUTIONS

IMPORTANT SAFETY INSTRUCTIONS

Read and understand all instructions. Failure to follow all instructions listed in this manual may result in electric shock, fire and/or personal injury. Save these instructions.
Never operate this unit when flammable materials or vapors are present because electrical devices produce arcs or sparks that can cause a fire or explosion. When using an electrical device, basic precautions should always be followed including the following section of this manual. Be sure to disconnect power supply before attempting to service or remove any components.
Never immerse electrical parts in water or any other liquid.
Avoid body contact with grounded surfaces when plugging and un-plugging this device in wet conditions.

ELECTRICAL INSTALLATION

Installation must be carried out by specialized personnel only, and must adhere to all local safety rules. As this unit can be supplied for different power supply versions, before connecting the unit to the power line, check if the voltage shown on the serial number tag corresponds to the one of your power supply.
This product uses grounded plugs and wires. Grounding provides a path of least resistance for electric current to reduce the risk of electric shock. This system is equipped with electrical cords that have ground wires internal to them and a grounding plug. The plug must be plugged into a matching outlet that is properly installed and grounded in accordance with all local codes and ordinances. Do not modify the plug provided, if it will not fit the outlet, have the proper outlet installed by a qualified electrician.

DO NOT ABUSE CORDS

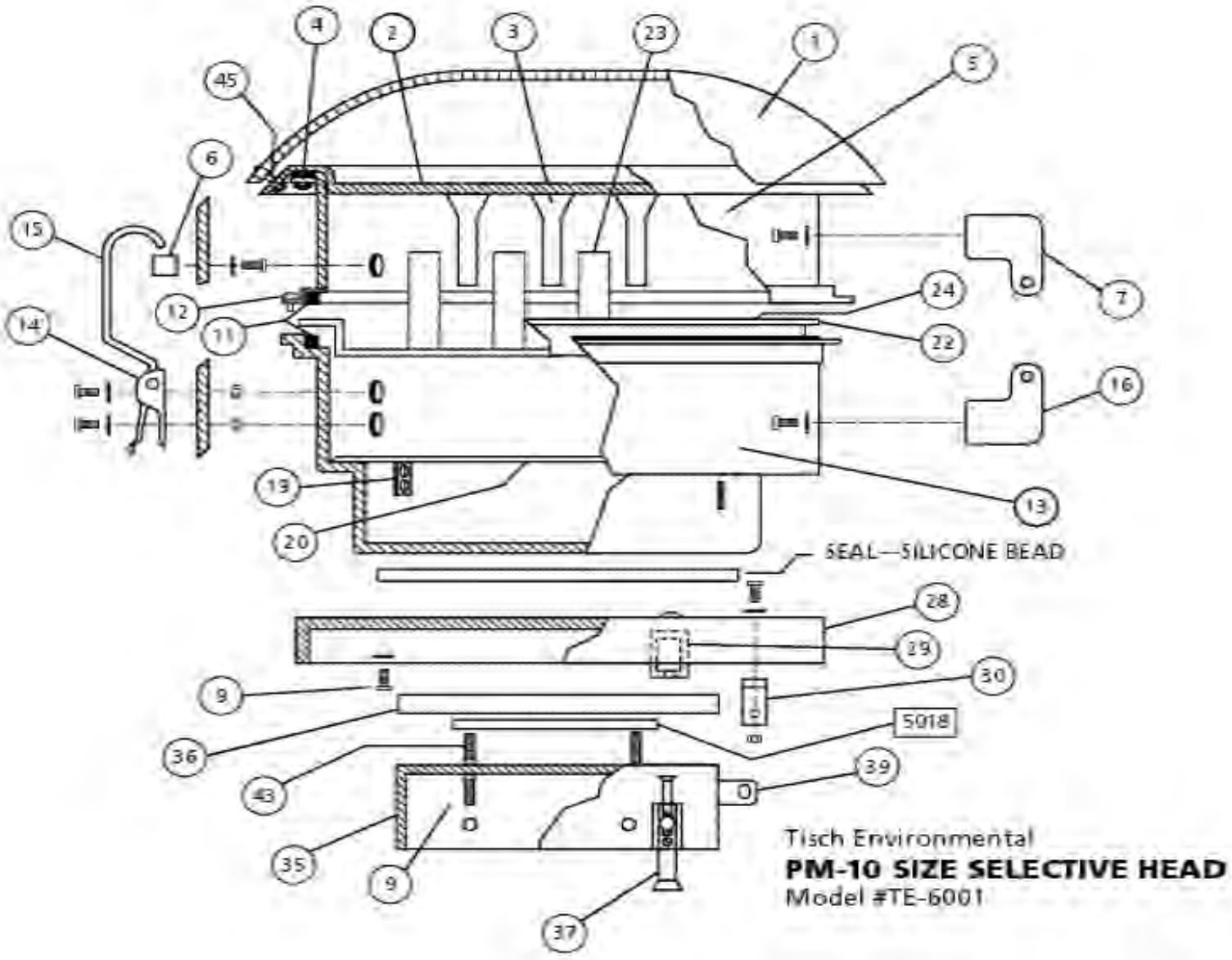
In the event any electrical component of this system is to be transported, DO NOT carry by its cord or unplug it by yanking the cord from the outlet. Pull plugs rather than cord to reduce the risk of damage. Keep all cords away from heat, oil, sharp objects, and moving parts.

EXTENSION CORDS

It is always best to use the shortest extension cord as possible. Grounded units require a three-wire extension cord. As the distance from the supply outlet increases, you must use a heavier gauge extension cord. Using extension cords with inadequately sized wire causes a serious drop in voltage, resulting in loss of power and possible damage to the equipment. It is recommended to only use 10-gauge extension cords for this product. Never use

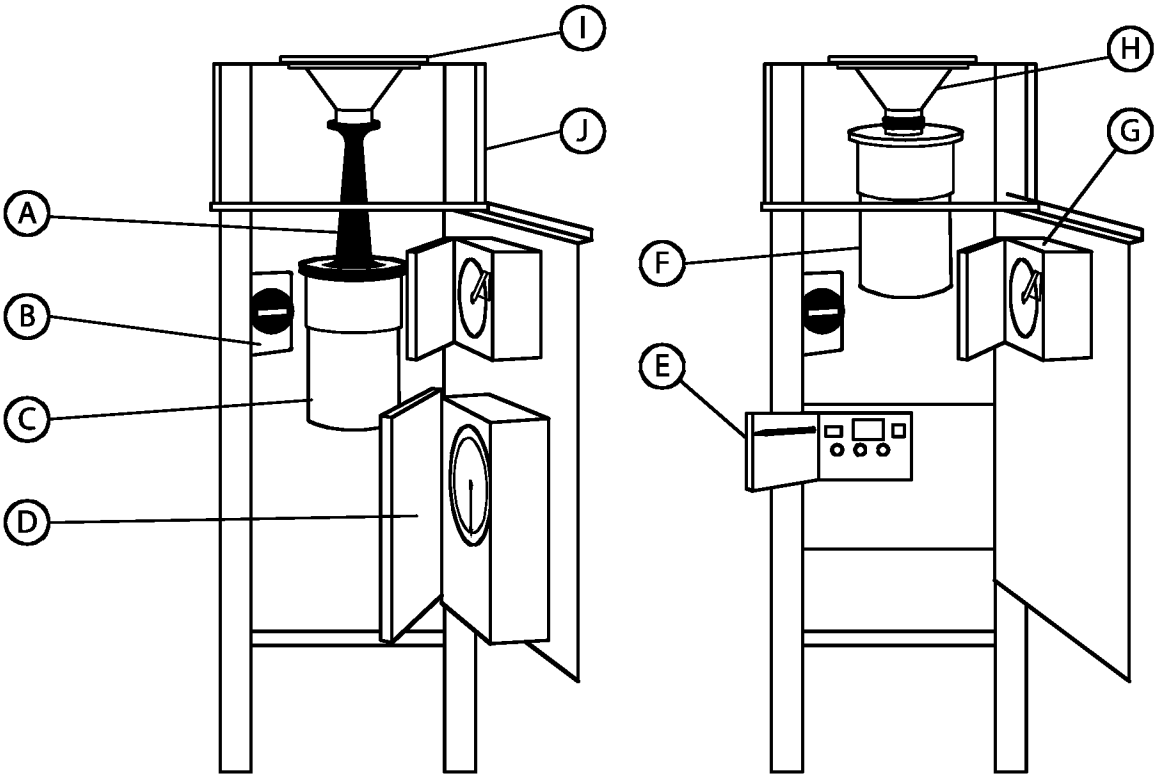
cords over one hundred feet. Outdoor extension cords are to be marked with the suffix “W-A” (“W” in Canada) to indicate that it is acceptable for outdoor use. Be sure your extension cord is properly wired and in good electrical condition. Always replace a damaged extension cord or have it repaired by a qualified person before using it. Protect your extension cords from sharp objects, excessive heat and damp or wet areas.

Schematic Diagram PM-10 Head TE-6001



Item No.	Part No.	Description
1.	TE-6001-1	Hood
2.	TE-6001-2	Acceleration Nozzle Plate with 9 nozzles
3.	TE-6001-3	Acceleration Nozzle
4.	TE-6001-4	Acceleration Nozzle Plate Gasket
5.	TE-6001-5	Top Tub Housing
6.	TE-6001-6	Top Tub Housing Strike
7.	TE-6001-7	Top Tub Housing Hinge
8.	TE-6001-8	Top Tub Housing Strut Holder Large
9.	TE-6001-9	Top Tub Housing Strut Holder Shoulder Bolt
10.	TE-6001-10	Strut
11.	TE-6001-11	Bead Gasket Strip (between tubs)
12.	TE-6001-12	Brass Alignment Pin Large
13.	TE-6001-13	Bottom Tub Housing
14.	TE-6001-14	Bottom Tub Housing Catch (no hook)
15.	TE-6001-15	Bottom Tub Housing Catch Hook
16.	TE-6001-16	Bottom Tub Housing Hinge
19.	TE-6001-19	Bug Screen Support Angle
20.	TE-6001-20	Bug Screen with edging
21.	TE-6001-21	Bug Screen black edging
22.	TE-6001-22	1st Stage Plate with 16 Vent Tubes
23.	TE-6001-23	1st Stage Plate Vent Tube
24.	TE-6001-24	Shim Plate
25.	TE-6001-25	Shim Plate Clips
26.	TE-6001-26	Spring for Shim Clips
27.	TE-6001-27	Small Brass Alignment Pin
28.	TE-6001-28	Inlet Base Pan
29.	TE-6001-29	Inlet Base Pan Strike
30.	TE-6001-30	Inlet Base Pan Hinge Bracket
31.	TE-6001-31	Inlet Base Pan Hinge Bracket Shoulder Bolt
32.	TE-6001-32	Inlet Base Pan Strut Bracket
35.	TE-6001-35	Shelter Base Pan
36.	TE-6001-36	Shelter Base Pan Gasket 16"x 16"
37.	TE-6001-37	Shelter Base Pan Catch with bolt
38.	TE-6001-38	Shelter Base Pan Catch Spacers
39.	TE-6001-39	Shelter Base Pan Hinge Bracket
40.	TE-6001-40	Shelter Base Pan Strut Holder Shoulder Bolt
43.	TE-6001-43	Brass Bolt Assembly with wing nuts
44.	TE-6001-44	Hood Spacers
45.	TE-6001-45	Hood Spacer Bag Complete
5018	TE-5018	8"x 10" Gasket

Schematic of PM-10 System–Lower Section



Model 6XXX-V
Volumetric Flow
Controlled PM-10

Model 6XXX
Mass Flow
Controlled PM-10

Item	Description
A	TE-10557 Volumetric Flow Controller
B	TE-5012 Elapsed Time Indicator
C	TE-5070 Volumetric Flow Controlled Blower Motor Assembly or TE-5070-BL Brush-less Blower Motor Assembly (not shown)
D	TE-5007 Mechanical Timer or TE-302 Digital Timer (not shown)
E	TE-300-310 Mass Flow Controller or TE-300-312 Digital Timer/Mass Flow Controller
F	TE-5005 Mass Flow Controlled Blower Motor Assembly or TE-5005-BL Brush-less Blower Motor Assembly (not shown)
G	TE-5009 Continuous Flow/Pressure Recorder
H	TE-6003 Filter Holder
I	TE-3000 Filter Media Holder/Filter Paper Cartridge 8″ x 10″
J	TE-6002 Anodized Aluminum Shelter

DESCRIPTION OF INSTRUMENTS

MODEL TE-6070 PM10 SYSTEM INCLUDES:
TE-5005 Blower Motor Assembly.
TE-300-310 Mass Flow Controller with 20 to 60 SCFM Air Flow Probe
TE-6003 PM10 8″ x 10″ Stainless Steel Filter Holder w/probe hole for MFC
TE-5007 7-Day Mechanical Timer
TE-5009 Continuous Flow/Pressure Recorder
TE-6001 Size Selective PM10 Inlet
TE-3000 Filter Media Holder/Filter Paper Cartridge 8″ x 10″
TE-5012 Elapsed Time Indicator
TE-6002 PM10 Anodized Aluminum Shelter

MODEL TE-6070-BL PM10 SYSTEM INCLUDES:
1) TE-5005-BL Brush-less Blower Motor Assembly
TE-300-310-BL Brush-less Mass Flow Controller with 20 to 60 SCFM Air Flow Probe
TE-6003 PM10 8″ x 10″ Stainless Steel Filter Holder w/probe hole for MFC
TE-5007 7-Day Mechanical Timer
TE-5009 Continuous Flow/Pressure Recorder
TE-6001 Size Selective PM10 Inlet
TE-3000 Filter Media Holder/Filter Paper Cartridge 8″ x 10″
TE-5012 Elapsed Time Indicator
TE-6002 PM10 Anodized Aluminum Shelter

MODEL TE-6070D PM10 SYSTEM SAME AS TE-6070 EXCEPT A DIGITAL TIMER IN PLACE OF A 7 DAY MECH. TIMER.
TE-5005 Blower Motor Assembly
TE-300-312 Combination Mass Flow Controller with 20 to 60 SCFM Air Flow Probe Digital Timer and Digital Elapsed Time Indicator
TE-6003 PM10 8″ x 10″ Stainless Steel Filter Holder w/probe hole for MFC
TE-5009 Continuous Flow/Pressure Recorder
TE-6001 Size Selective PM10 Inlet
TE-3000 Filter Media Holder/Filter Paper Cartridge 8″ x 10″
TE-6002 PM10 Anodized Aluminum Shelter

MODEL TE-6070D-BL PM10 SYSTEM SAME AS TE-6070-BL EXCEPT DIGITAL TIMER IN PLACE OF A 7 DAY MECH. TIMER.
TE-5005-BL Brush-less Blower Motor Assembly
TE-300-310-BL Brush-less Mass Flow Controller with 20 to 60 SCFM Air Flow Probe
TE-6003 PM10 8″ x 10″ Stainless Steel Filter Holder w/probe hole for MFC
TE-302 Solid State Digital Timer Programmer w/Digital E.T.I.
TE-5009 Continuous Flow/Pressure Recorder
TE-6001 Size Selective PM10 Inlet
TE-3000 Filter Media Holder/Filter Paper Cartridge 8″ x 10″
TE-6002 PM10 Anodized Aluminum Shelter

MODEL TE-6070V PM10 SYSTEM INCLUDES:
TE-5070 Blower Motor Assembly For VFC System
TE-10557 PM10 Volumetric Flow Controller w/Flow Look Up Table
TE-6003V PM10 8″ x 10″ Filter Holder w/Stagnation Pressure Tap
TE-5007 7-Day Mechanical Timer
TE-5009 Continuous Flow/Pressure Recorder
TE-6001 Size Selective PM10 Inlet
TE-3000 Filter Media Holder/Filter Paper Cartridge 8″ x 10″
TE-5012 Elapsed Time Indicator
TE-6002 PM10 Anodized Aluminum Shelter
TE-5030 30″ Slack Tube Water Manometer 15″-0-15″

MODEL TE-6070V-BL PM10 SYSTEM INCLUDES:
TE-5070BL Brush-less Blower Motor Assembly for VFC System
TE-10557-PM10-BL Volumetric Flow Controller w/Flow Look Up Table
TE-6003V PM10 8″ x 10 Filter Holder w/Stagnation Pressure Tap
TE-5007 7-Day Mechanical Timer
TE-5009 Continuous Flow/Pressure Recorder
TE-6001 Size Selective PM10 Inlet
TE-3000 Filter Media Holder/Filter Paper Cartridge 8″ x 10″
TE-5012 Elapsed Time Indicator
TE-6002 PM10 Anodized Aluminum Shelter
TE-5030 30″ Slack Tube Water Manometer 15″-0-15″
TE-10965 Step up Transformer 110v to 220v VFC Motor

MODEL TE-6070DV PM10 SYSTEM SAME AS TE-6070V EXCEPT A DIGITAL TIMER IN PLACE OF 7 DAY MECH. TIMER.
TE-5070 Blower Motor Assembly for VFC System
TE-10557 PM10 Volumetric Flow Controller w/Flow Look Up Table
TE-6003V PM10 8″ X 10″ Filter Holder w/Stagnation Pressure Tap
TE-302 Solid State Digital Timer Programmer w/Digital E.T.I.
TE-5009 Continuous Flow/Pressure Recorder
TE-6001 Size Selective PM10 Inlet
TE-3000 Filter Media Holder/Filter Paper Cartridge 8″ X 10″
TE-6002 PM10 Anodized Aluminum Shelter
TE-5030 30″ Slack Tube Water Manometer 15″-0-15″

MODEL TE-6070DV-BL PM10 SYSTEM SAME AS TE-6070V-BL EXCEPT DIGITAL TIMER IN PLACE OF 7 DAY MECH. TIMER.
TE-5070-BL Brush-less Blower Motor Assembly for VFC System
TE-10557-PM10-BL Volumetric Flow Controller w/Flow Look Up Table
TE-6003V PM10 8″ x 10″ Filter Holder w/Stagnation Pressure Tap
TE-302 Solid State Digital Timer Programmer w/Digital E.T.I.
TE-5009 Continuous Flow/Pressure Recorder
TE-6001 Size Selective PM10 Inlet
TE-3000 Filter Media Holder/Filter Paper Cartridge 8″ x 10″
TE-6002 PM10 Anodized Aluminum Shelter
TE-5030 30″ Slack Tube Water Manometer 15″-0-15″
TE-10965 Step up Transformer 110v to 220v VFC Motor

MODEL TE-6000 PM10 SYSTEMS SAME AS TE-6070 EXCEPT DIGITAL TIMER AND AUTO DOWNLOAD.
TE-5005 Blower Motor Assembly
TE-300 Combination Mass Flow Controller with 20 to 60 SCFM Air Flow Probe, Electronic Timer and Auto Down Load
TE-6003 PM10 8″ x 10″ Stainless Steel Filter Holder w/probe hole for MFC
TE-5009 Continuous Flow/Pressure Recorder
TE-6001 Size Selective PM10 Inlet
TE-3000 Filter Paper Media Holder/Filter Paper Cartridge 8″ x 10″
TE-5012 Elapsed Time Indicator
TE-6002 PM10 Anodized Aluminum Shelter

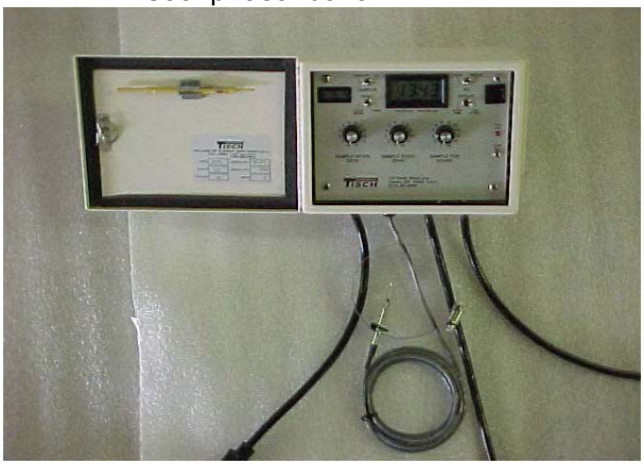
EXPLANATION OF INDICATORS, DISPLAYS, AND CONTROLS

TE-300-310 Mass Flow Controller with 20 to 60 SCFM Air Flow Probe. Controls a constant flow rate through, 8″ x 10″ Filter Media (TE-QMA Micro Quartz Filter Media Required for PM10). See Photo Below.

TE-300-310-BL Brush-less Mass Flow Controller with 20 to 60 SCFM Air Flow Probe.

Controls a constant flow rate through, 8″ x 10″ Filter Media (TE-QMA Micro Quartz Filter Media Required for PM10). This product is similar to above flow controller in size, shape and operation.

TE-300-312 Combination Mass Flow Controller w/20 to 60 SCFM Air Flow Probe,Digital Timer and Digital Elapsed Time Indicator. Controls a constant Flow rate through 8″ x 10″ Filter Media (TE-QMA Micro Quartz Filter Media required for PM10) Also turns sampler on/off at precise times while registering elapsed time on a re-settable digital E.T.I. See photo below



TE-10557 PM10 Volumetric Flow Controller w/Look Up Table. Controls a Constant Flow through, 8″ x 10′ Filter Media (TE-QMA Micro Quartz Filter Media required for PM10). See Photo Below.

TE-10557 PM10-BL Brushless Volumetric Flow Controller w/Look Up Table. Controls a Constant Flow through, 8″ x 10′ Filter Media (TE-QMA Micro Quartz Filter Media required or PM10). See Photo Below

TE-5012 Elapsed Time Indicator Mechanical E.T.I. registers how long the PM10
System ran (non re-settable) 00000.00 hours and tenths of hour.

TE-5013 Elapsed Time Indicator Mechanical E.T.I. Registers how long the PM10 System ran 0000.0 minutes. Similar to TE-5012 ETI except this product features a re-settable clock.

TE-3000 Filter Media Holder/Filter Paper Cartridge facilitates the changing of filters by keeping contamination off the clean filter and protects the particulate on the filter from being disturbed during transit. Shown in photo below on top of TE-6003.

TE-6003 PM10 Stainless Steel 8” x 10” Filter Holder used with Mass Flow Controller PM10 System. Filter Holder has a Probe Hole for 20 to 60 SCFM MFC Flow Probe.

TE-6002 PM10 Anodized Aluminum Shelter for all Tisch Environmental PM10 Systems. This Shelter supports the PM10 Size Selective Inlet. Also protects the other components of the PM10 System.

TE-6003V PM10 Stainless Steel 8” x 10” Filter Holder used with Volumetric Controlled PM10 System. Filter Holder has a Stagnation Pressure Tap to measure Pressure Drop across the Filter Paper. Similar to TE-6003 pictured above with the stagnation pressure tap located on the side.

TE-10965 Step up transformer used with Model TE-6070V-BL, TE-6070DV-BL PM10 system. Not Pictured

TE-5030 30" Slack Tube Water Manometer 15"-0-15", used to measure flow rate.

Filling Instructions:

- Using 1 quart distilled water, add ¾ oz. bottle of TE-10255 Fluorescent green color concentrate.
- Remove a tubing connector from the manometer and pour fluid in to mid-point level.
- Shake to remove air bubbles and slide scale so zero is in line with the meniscus of the two fluid columns.

For readings in inches of mercury, fill with 13.6 SP. GR. triple distilled mercury. When used with mercury, some discoloration of the vinyl tubing will normally occur.

Reading the Slack Tube Manometer:

- Connect the manometer to the source of pressure, vacuum or differential pressure. When the pressure is imposed add the number of inches one column travels up to the amount the other column travels down to obtain the pressure reading.
- Should one column travel further than the other column, due to minor variations in tube I.D. or to pressure imposed, the accuracy of the pressure reading thus obtained is not impaired. The U-tube Manometer is a primary measuring device indicating pressure by the difference in the height of two columns of fluid. The fact that one column travels further than the other does not affect the accuracy of the reading.

TE-5005-BL Blower Motor Assembly (Brushless Type with 5-wire connector) used with Mass Flow Controlled PM10 System.

TE-5070-BL Blower Motor Assembly (Brushless Type with 3-wire connector) used with Volumetric Flow Controlled PM0 Systems.

TE-5005 Blower Motor Assembly (Brush Type) used with Mass Flow Controller PM10 System.

TE-5070 Blower Motor Assembly (Brush Type) used with Volumetric Flow Controlled PM0 Systems.

TE-5028 Variable Resistance Calibration Kit. This model is recommended for all Tisch Environmental PM10 Systems. Included: Variable Orifice, NIST Traceable Calibration Certificate, Adapter Plate, Slack Tube Manometer, Tubing and Carrying Case.

TE-5007 Seven Day Mechanical Timer, used to turn sampler on and off at selected times.

PROGRAMMING INSTRUCTIONS

1) To Set “ON” Times, Place Bright ON Trippers Against Edge of Clock-Dial At Day-of-Week And Time-of-Day When “ON” Operations Are Desired. Tighten Tripper Screws Securely.
2) To Set “OFF” Times, Place Dark OFF Trippers Against Edge of Clock-Dial At Time When “OFF” Operations Are Desired. Tighten Tripper Screws Securely.
3) To Skip Days, Omit Trippers for The Day(s) Automatic Operations Is/Are Not Required.
4) To Set Dial To Time-Of-Day, Turn Dial Clockwise And Align The Exact Day-of-Week And Time-of-Day (AM OR PM) On Dial With The Time Pointer. Some Allowance May Be Required To Compensate for Gear Backlash.

CAUTION: DO NOT MOVE POINTER OR FORCE DIAL COUNTERCLOCKWISE

OPERATING INSTRUCTIONS

- To Operate Switch Manually: Move Manual Lever Below Clock-Dial Left or Right as Indicated by Arrows. This Will Not Affect Next Automatic Operation.

- In Case of Power Failure or to Advance/Retard Time: Reset Time-Of-Day
  See Step 4 of Programming Instructions.

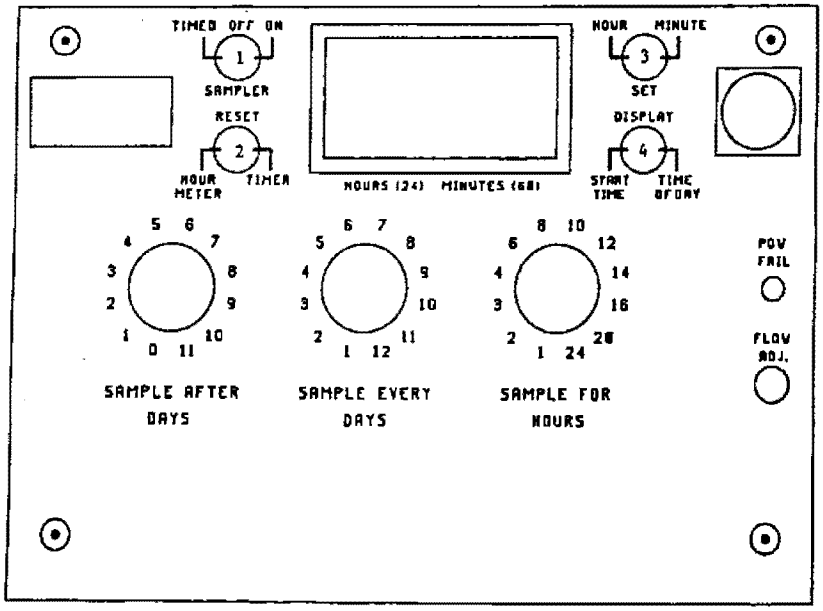
TE-300-313 Combination Mass Flow Controller with 20 to 60 SCFM Air Flow Probe, 7- Day Mechanical On-Off Timer and Elapsed Time Indicator. Controls a constant Flow Rate through 8″ x 10″ Filter Media (TE-QMA Micro Quartz Filter Media Required for PM10) Also turns sampler on and off while registering elapsed time. This product has the outside appearance of the TE-5007 timer with the controller and ETI integral to the design.

TE-302 Digital Timer/Elapsed Time Indicator, used to turn sampler on and off at selected times, and to record elapsed time.

Operating Instructions for TE-302 Digital Timer

To set up the digital timer:

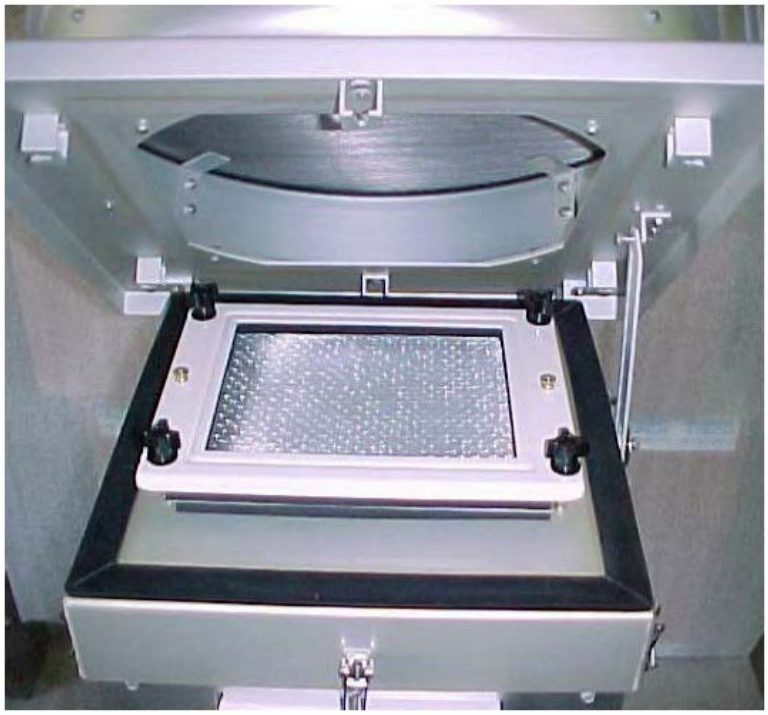
- Start with the Sampler Switch (Timed – Off – On) Switch #1, in the Off position.
- If you need to test or adjust the blower motor turn the Sampler switch to On. When done with adjusting, turn it back to Off.
- Place the rotary switches in the desired positions.
- If today is Friday and you want the first sample time on Sunday, turn the "Sample After Days" switch to position 2.
- If you want to run the sampler every Sunday after that, turn the "Sample Every Days" switch to position 7, (for six day sampling use position 6).
- Turn "Sample for Hours" to desired number of running hours.
- Next put the Display switch, Switch #4, in the Start Time position.
- Then using the Set switch, Switch #3, enter the start time, hours and minutes.
- Next put the Display switch, Switch #4, in the Time of Day position.
- Then using the Set switch, Switch #3, enter the current time, hours and minutes.
- Now press and release the Reset switch, Switch #2, toward Timer. A small triangle on the display will start blinking. This indicates the timer is running.
- If you need to reset the Hour Meter to zero.
- Press and release the reset switch, Switch #2, twice, toward Hour Meter.
- Last thing to do is place the Sampler switch, Switch #1, (Timed – Off – On) in the Timed position



TE-6001 Size Selective PM10 Inlet (cut point less than 10 micron) Precision Symmetrical Designed Inlet insures wind direction insensitivity. Large particles are impacted on a greased shim plate. Particles smaller than 10 microns are collected on the 8″ x 10″ Quartz Filter.

TE-6001 Closed

TE-6001 Open Position



TE-6001 Shown raised over shelter to expose filter cartridge.

SETUP & INSTALLATION INSTRUCTIONS – MASS FLOW CONTROLLED SYSTEMS TE-6070, TE-6070D, TE-6070BL, TE-6070D-BL

UNPACKING & ASSEMBLY

1. Shelter Box - 46" x 20" x 23" 74 lbs

TE-6070	Anodized Aluminum Shelter with mounted Flow Controller, Timer and TE-5009 Continuous Flow Recorder
TE-5005	Blower Motor Assembly with tubing, or brush-less blower
TE-6003	8″ x 10″ PM10 Stainless Steel Filter Holder with probe hole
TE-5005-9	Filter Holder Gasket
TE-3000	Filter Paper Cartridge
Envelope	with TE-106 box of charts, and operations manual

2. Inlet Box - 32" x 32" x 26" 56 lbs

TE-6001 Size Selective Inlet

***** Save the shipping containers and packing material for future use.**

1. Remove all items from the boxes.

2. Enclosed in the 13" x 10" x 9" box on bottom of shelter is the TE-5005 Blower Motor Assembly. Enclosed in the 13″ x 10″ x 9″ box inside of shelter is the Filter Holder with TE-5005-9 gasket and TE-3000 Filter Paper Cartridge. Remove from boxes.

3. Screw TE-5005 Blower Motor Assembly onto the Filter Holder (tubing, power cord, and hole in filter holder collar to the right) make sure TE-5005-9 gasket is in place.

4. Lift TE-6001 SSI, hood, and hood spacer bag from carton and place on table.

5. Remove cable tie on bottom of SSI that is holding strut and remove shoulder bolt and large washer.

6. Align middle of strut with hole in spacer and fasten with shoulder bolt and large washer, make sure large washer is on top of strut.

7. Place SSI on shelter and align shelter base pan 10-24 nutsert holes with holes in side of shelter and insert four 10-24 x 1″ bolts.

   CAUTION: Before opening SSI, be sure that shelter is securely mounted to ground or floor. Use of out riggers to secure vertical orientation is strongly recommended.

8. Place SSI hood onto acceleration nozzle plate (top of SSI).

9. Locate hood spacer between hood and acceleration nozzle plate and loosely fasten with 10-32 x ½″ thumb bolt, making sure plastic washer is in place. Do this loosely for all eight hood spacers, before tightening.

10. Open TE-6001 SSI by disengaging hooks and lifting the middle section into the open position. Remove cardboard and rubber bands that are covering filter holder assembly opening.

11. Place Blower Motor Assembly on top of Inlet Base Plate. Locate Mass Flow Probe. Take Flow Controller probe and insert into filter holder collar. Before tightening be certain probe slot is positioned so air coming into filter holder goes through the open section and flows across the ceramic element.

12. Lower filter holder assembly down through opening, making sure 8″ x 10″ gasket is under filter holder.

13. Put TE-3000 Filter Paper Cartridge on top of filter holder and align the brass bolt assembly with the cartridge. Tighten for airtight seal.

    IMPORTANT: Remove cover on top of TE-3000 Filter Paper Cartridge before turning on the sampler. The cover is only used to protect sample from contamination during transport.

14. Close Inlet, making sure of an airtight seal.

15. Connect tubing from pressure tap of blower motor to TE-5009 Flow Recorder.

16. Before operating, make sure TE-6001-24 Shim Plate has been wiped clean and then treated with Dow Corning Silicone spray 316, evenly. See Sampler Operation)

SETUP & INSTALLATION INSTRUCTIONS – VOLUMETRIC FLOW CONTROLLED SYSTEMS TE-6070V, TE-6070DV, TE-6070V-BL, TE-6070DV-BL

UNPACKING & ASSEMBLY

1. Shelter Box 46″ x 20″ x 23″ 50 lbs

TE-6070V/BL	Anodized Aluminum Shelter with mounted Continuous Flow Recorder and Timer on door with Elapsed Time Indicator.
Envelope	Contents: TE-106 charts, and operations manual.

2. VFC parts box 28″ x 21″ x 10″ 20 lbs

TE-5030	30″ Water Manometer with VFC Fitting
TE-5070	VFC Blower Motor Assembly, or Brush-less Motor
TE-10557PM10	Volumetric Flow Controller PM10, or Brush-less
TE-6003V	8″ x 10″ VFC PM10 Stainless Steel Filter Holder

3. Inlet Box - 32″ x 32″ x 26″ 56 lbs

TE-6001 Size Selective Inlet

***** Save the shipping containers and packing material for future use.**

1. Lift SSI, hood, and hood spacer bag from carton and place on table.

2. Remove cable tie on bottom of SSI that is holding strut and remove shoulder bolt and large washer.

3. Align middle of strut with hole in spacer and fasten with shoulder bolt and large washer, make sure large washer is on top of strut.

4. Place SSI on shelter and align shelter base pan 10-24 nutsert holes

with holes in side of shelter and insert four 10-24 x 1″ bolts.

CAUTION: Before opening SSI, be sure that shelter is securely mounted to ground or floor. Use of out riggers to secure vertical orientation is strongly recommended.

5. Place SSI hood onto acceleration nozzle plate (top of SSI).

6. Locate hood spacer between hood and acceleration nozzle plate and loosely fasten with 10-32 x ½″ thumb bolt, making sure plastic washer is in place. Do this loosely for all eight hood spacers, before tightening.

7. Open TE-6001 SSI by disengaging hooks and lifting the middle section into the open position. Remove cardboard and rubber bands that are covering filter holder assembly opening.

8. Screw Filter Holder on to VFC Device, be sure gasket is in place.

9. Lower filter holder assembly down through opening, making sure 8″ x 10″ gasket is under filter holder.

10. Put TE-3000 Filter Paper Cartridge on top of filter holder and align the brass bolt assembly with the cartridge. Tighten for airtight seal.

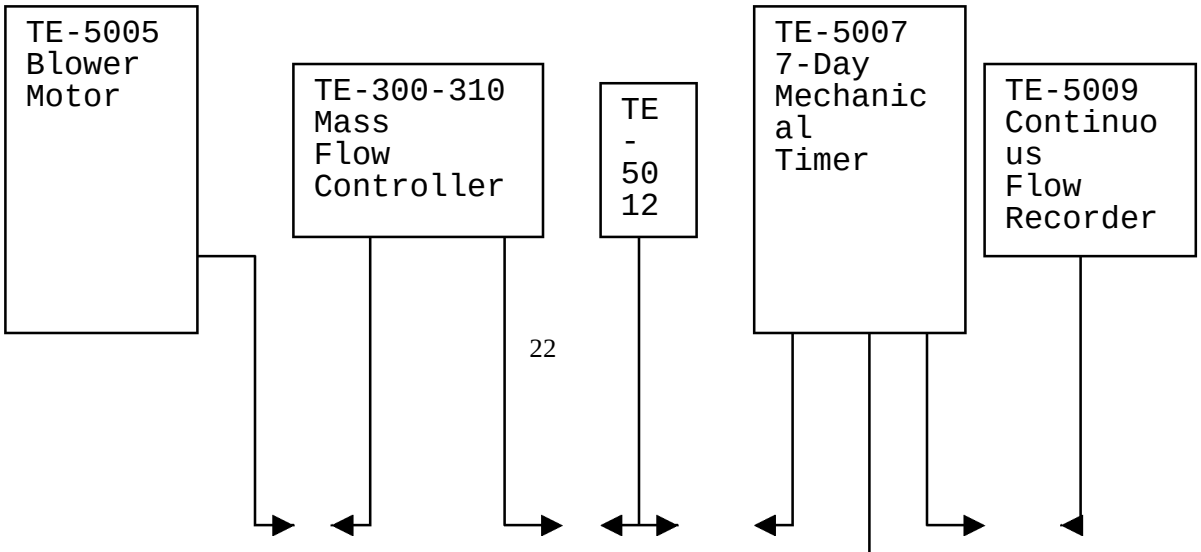
    IMPORTANT: Remove cover on top of TE-3000 Filter Paper Cartridge before turning on sampler. The cover is only used to protect sample from contamination during transport.

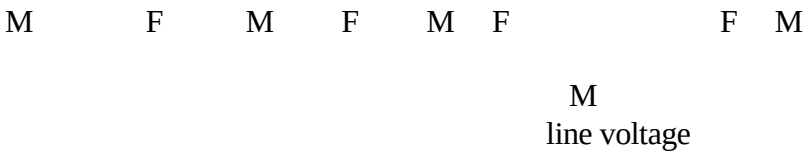
11. Connect clear piece of tubing from inside of shelter on to brass pressure tap located on the filter holder side.

12. Close Inlet, making sure of an airtight seal.

13. Before operating, make sure TE-6001-24 Shim Plate has been wiped clean and then treated with Dow Corning Silicone spray 316, evenly. (See Sampler Operation)

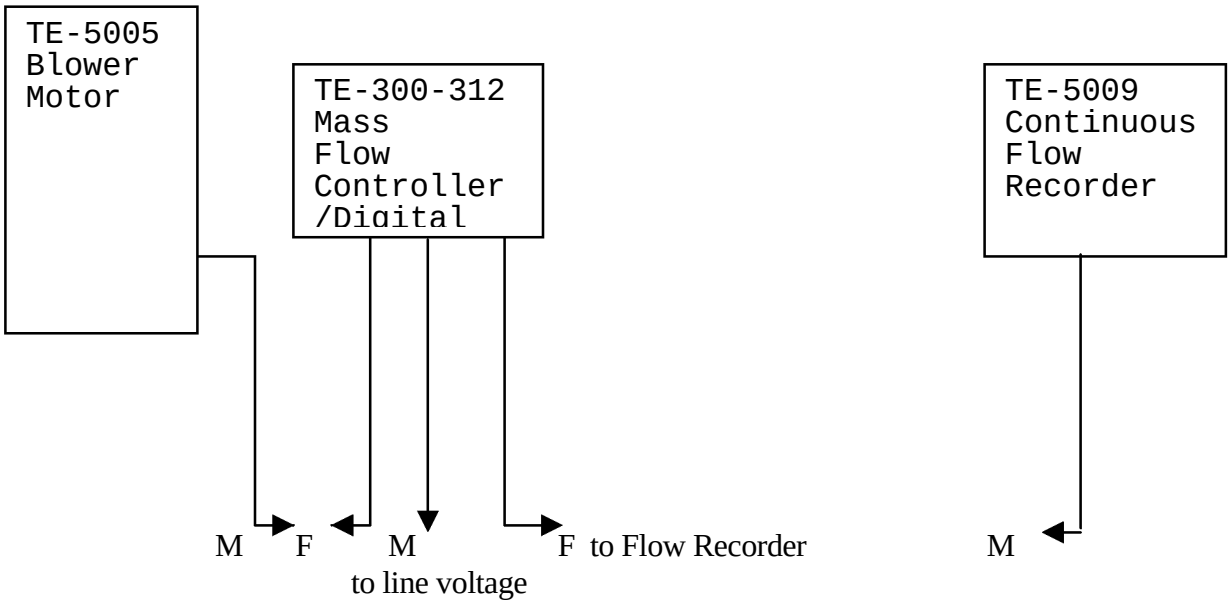
ELECTRICAL HOOK-UP TE-6070





The TE-5005 Blower Motor male cord set plugs into the TE-300-310 Mass Flow Controller Female cord set.
The Mass Flow Controller male cord set plugs into the TE-5012 Elapsed Time Indicator female side.
The male side of the ETI cord set plugs into the TE-5007 7-Day Mechanical Timer timed female cord set which is on the left side of timer.
The other female cord set on timer (on the right) is hot all the time and plugs into the TE-5009 Continuous Flow Recorder male cord set.
The male cord set of timer plugs into the line voltage.

ELECTRICAL HOOK-UP TE-6070-D

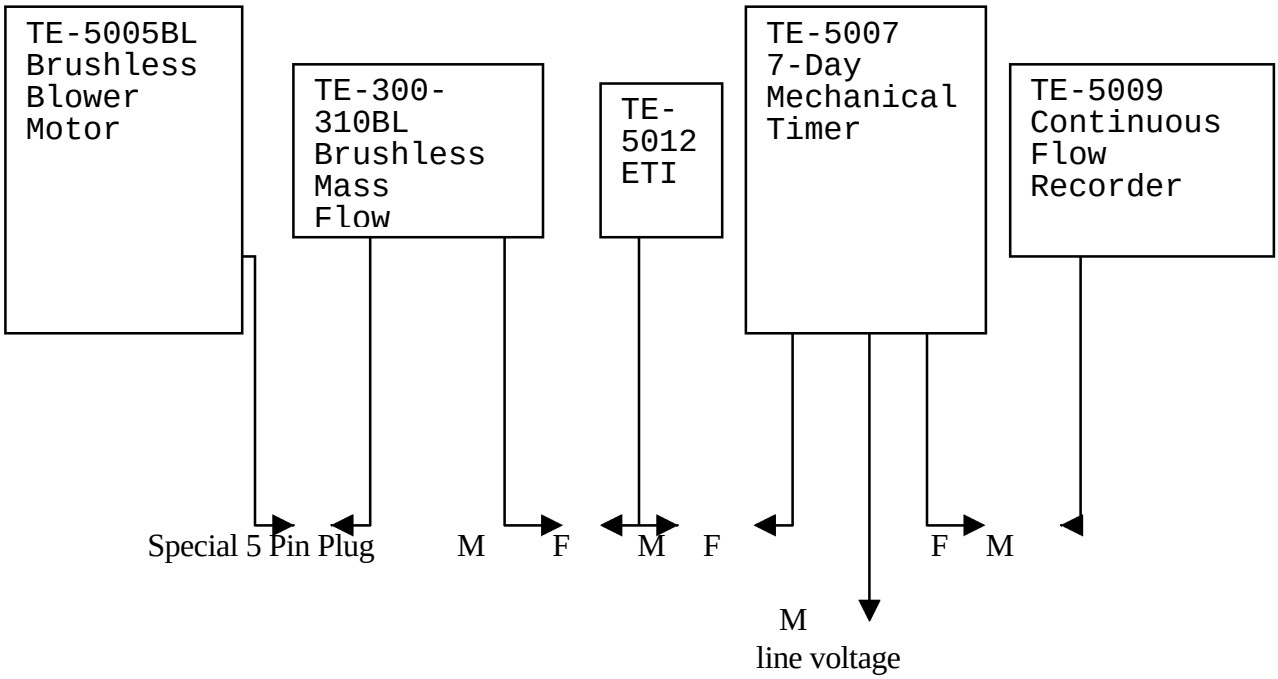


The TE-5005 Blower Motor male cord set plugs into the TE-300-312 Mass Flow Controller/ Digital Timer/ETI left Timed Female cord set.

The Mass Flow Controller/Digital Timer/ETI male cord set plugs into the line voltage.

The Mass Flow Controller/Digital Timer/ETI right female cord set is hot at all times and plugs into the TE-5009 Continuous Flow Recorder male cord set.

ELECTRICAL HOOK-UP TE-6070-BL



The TE-5005BL Brushless Blower Motor special 5 pin male cord set plugs into the special 5 pin female cord set on the TE-300-310BL Brushless Mass Flow Controller.

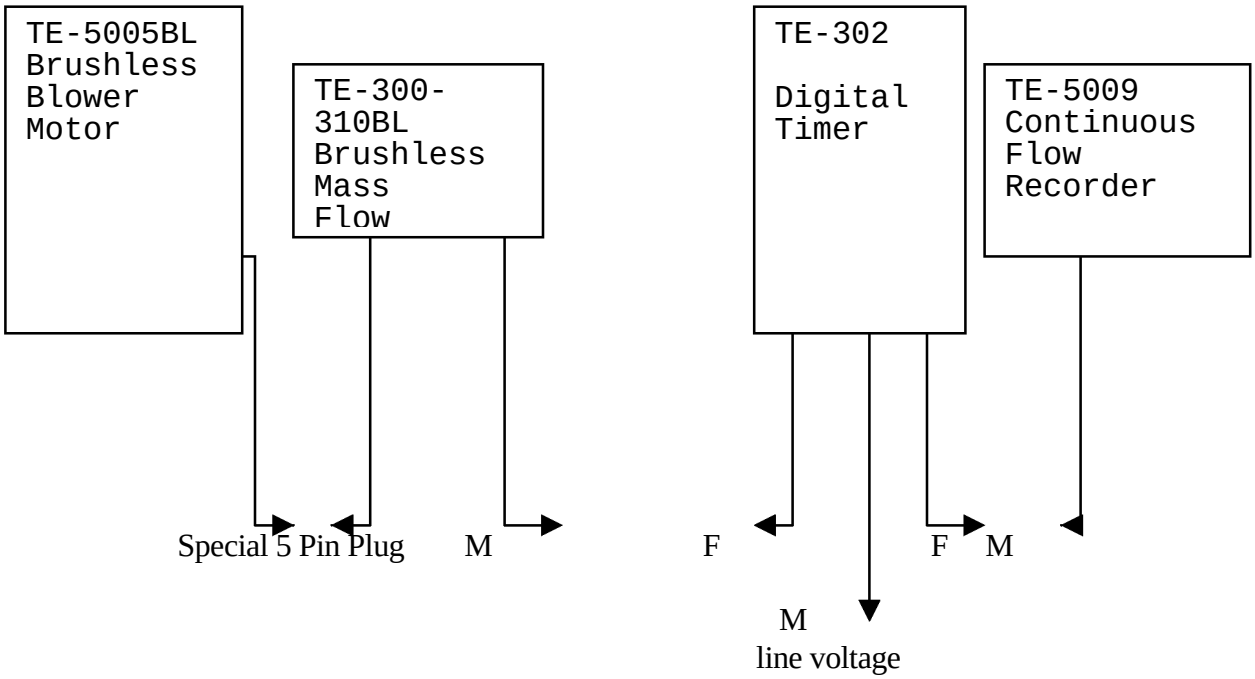
The Brushless Mass Flow Controller male cord set plugs into the TE-5012 Elapsed Time Indicator female side.

The male side of the ETI cord set plugs into the TE-5007 7-Day Mechanical Timer timed female cord set which is on the left side of timer.

The other female cord set on timer (on the right) is hot all the time and plugs into the TE-5009 Continuous Flow Recorder male cord set.

The male cord set of timer plugs into the line voltage.

ELECTRICAL HOOK-UP TE-6070-D-BL



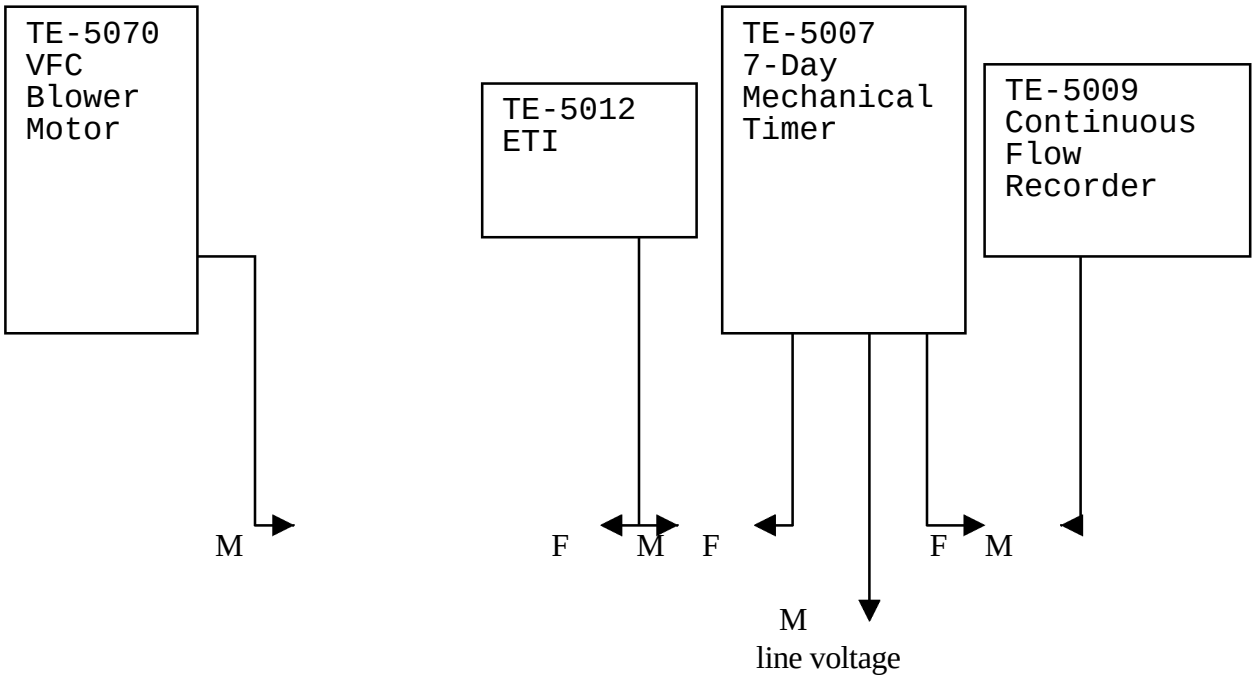
The TE-5005BL Brushless Blower Motor special 5 pin male cord set plugs into the special 5 pin female cord set on the TE-300-310BL Brushless Mass Flow Controller.

The Brushless Mass Flow Controller male cord set plugs into the TE-302 Digital Timer timed female cord set which is on the left side of timer.

The other female cord set on the digital timer (on the right) is hot all the time and plugs into the TE-5009 Continuous Flow Recorder male cord set.

The male cord set of the digital timer plugs into the line voltage.

ELECTRICAL HOOK-UP TE-6070V



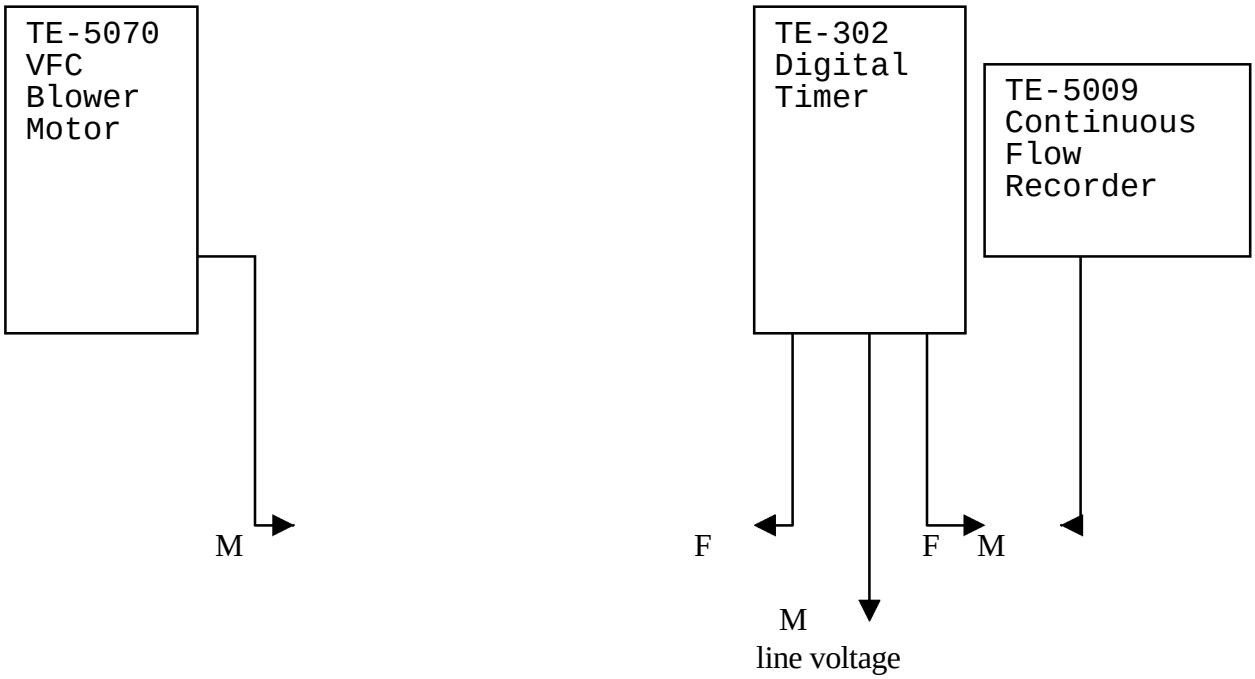
The TE-5070 VFC Blower Motor male cord set plugs into the TE-5012 Elapsed Time Indicator female side.

The male side of the ETI cord set plugs into the TE-5007 7-Day Mechanical Timer timed female cord set which is on the left side of timer.

The other female cord set on timer (on the right) is hot all the time and plugs into the TE-5009 Continuous Flow Recorder male cord set.

The male cord set of timer plugs into the line voltage.

ELECTRICAL HOOK-UP TE-6070-DV

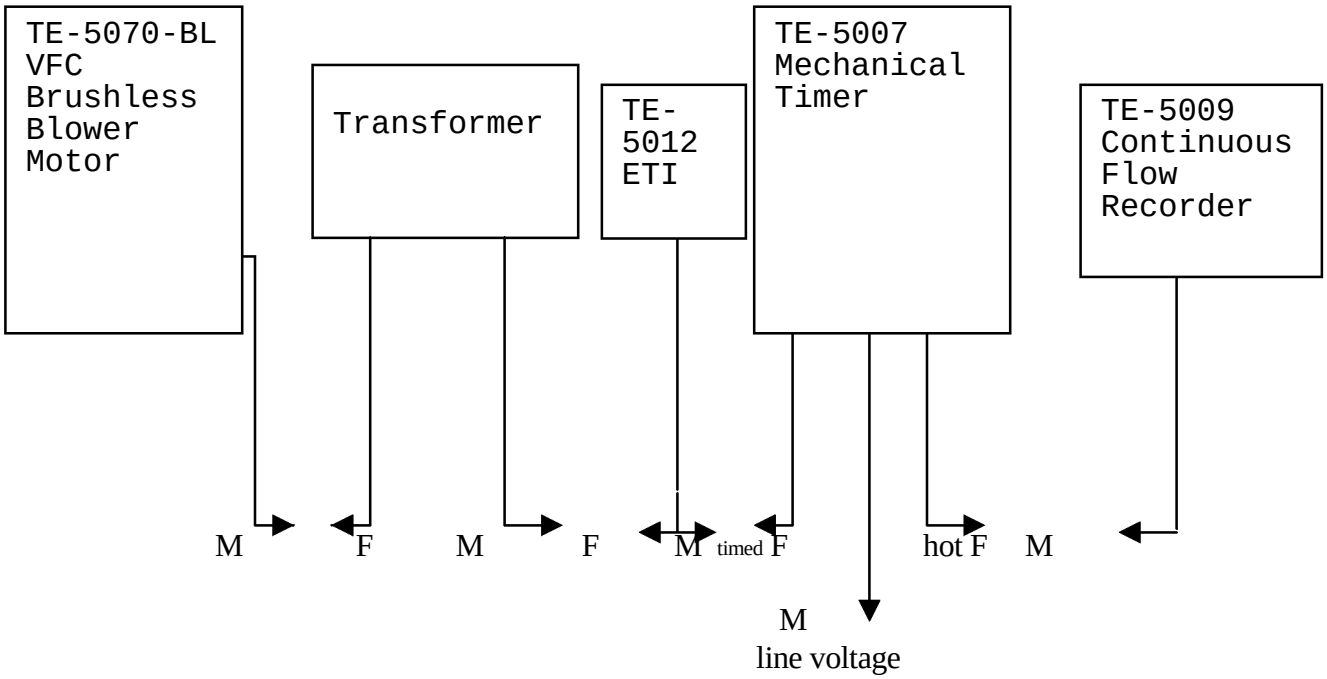


The TE-5070 VFC Blower Motor male cord set plugs into the TE-302 Digital Timer timed female cord set which is on the left side of timer.

The other female cord set on timer (on the right) is hot all the time and plugs into the TE-5009 Continuous Flow Recorder male cord set.

The male cord set of timer plugs into the line voltage.

ELECTRICAL HOOK-UP TE-6070V-BL



The TE-5070-BL Brushless Blower Motor male cord set plugs into the Transformer Female cord set.

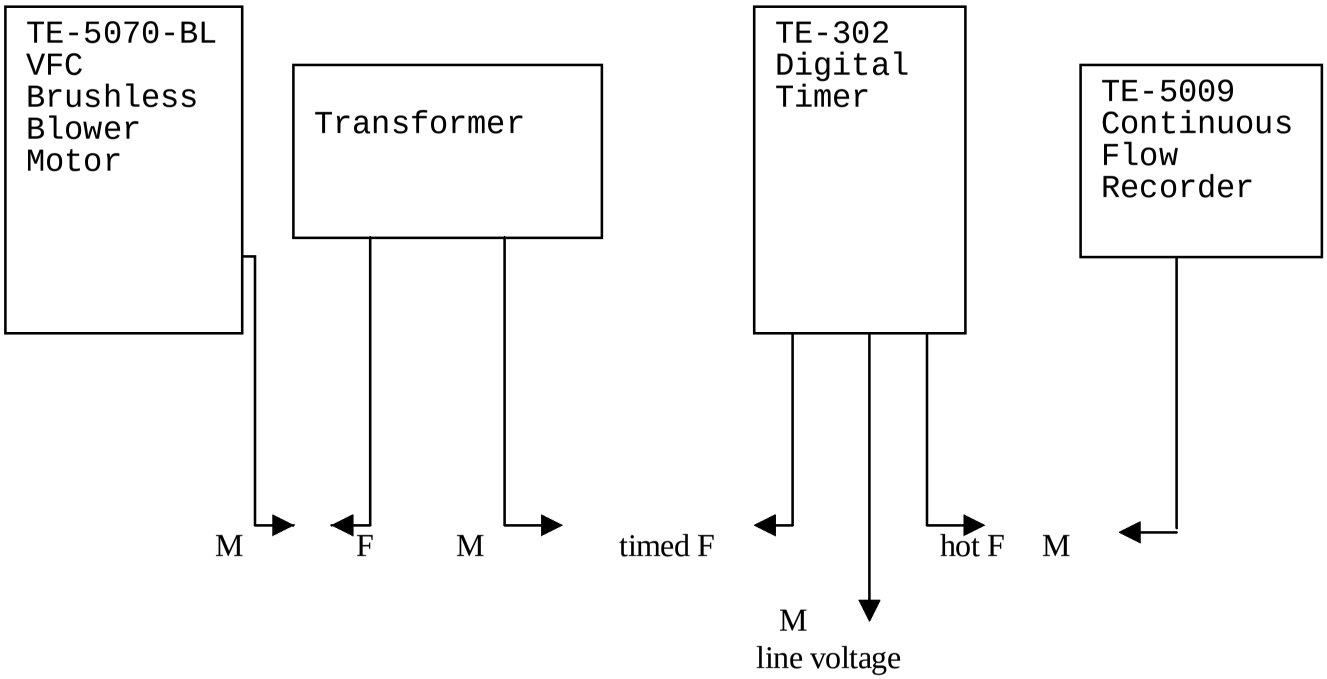
The Transformer male cord set plugs into the TE-5012 ETI female end.

The male side of TE-5012 ETI plugs into the left timed female of the TE-5007 Mechanical Timer.

The other female cord set on timer (on the right) is hot all the time and plugs into the TE-5009 Continuous Flow Recorder male cord set.

The male cord set of timer plugs into the line voltage.

ELECTRICAL HOOK-UP TE-6070-DV-BL



The TE-5070-BL Brushless Blower Motor male cord set plugs into the Transformer Female cord set.

The Transformer male cord set plugs into the TE-302 Digital Timer timed female cord set which is on the left side of timer.

The other female cord set on timer (on the right) is hot all the time and plugs into the TE-5009 Continuous Flow Recorder male cord set.

The male cord set of timer plugs into the line voltage.

GENERAL CALIBRATION REQUIREMENTS

PM10 High Volume Air Samplers should be calibrated:

1. Upon installation

2. After any motor maintenance

3. Once every quarter (three months)

4. After 360 sampling hours

"Note" for supplemental guidance reference EPA's Quality Assurance Handbook Section 2.11 also Appendix J located at end of this manual.

CALIBRATION KITS

The two types of calibration kits available for PM10 High Volume Air Samplers are the TE-5025 and the TE-5028.

The TE-5025 utilizes five resistance plates to simulate various filter loading conditions. The TE-5025 calibration kit includes: carrying case, 30” slack tube water manometer, adapter plate, 3’ piece of tubing, TE-5025A orifice with flow calibration certificate, and 5 load plates (5,7,10,13,18).

The TE-5028 is the preferred method to calibrate PM10 High Volume Air Samplers. It simulates change in the resistance by merely rotating the knob on the top of the calibrator. The infinite resolution lets the technician select the desired flow resistance. The TE-5028 calibration kit includes: carrying case, 30” slack tube water manometer, adapter plate, 3’ piece of tubing, and TE-5028A orifice with flow calibration certificate.

Each TE-5025A and TE-5028A is individually calibrated on a primary standard positive displacement device, which is directly traceable to NIST.

** It is recommended by USEPA that each calibrator should be re-calibrated annually for accuracy and reliability.

CALIBRATION PROCEDURE-Mass Flow Controlled TE-6070, TE-6070D

The following is a step-by-step process for the calibration of **TE-6070, TE-6070D Mass Flow Controlled PM10 High Volume Sampling Systems.** Following these steps are example calculations determining the calibration flow rates, and resulting slope and intercept for the sampler. These instructions pertain to the samplers that have flow controlled by electronic mass flow controllers (MFC) in conjunction with a continuous flow recorder. This calibration differs from that of a volumetric flow controlled sampler. The attached example calibration worksheets can be used with either a **TE-5025 Fixed Orifice Calibrator** that utilize resistance plates to simulate a variation in airflow or a **TE-5028 Variable Orifice Calibrator** which uses an adjustable or variable orifice. The attached worksheet uses a variable orifice. Either type of orifice is acceptable for calibrating high volume samplers the calibration process remains the same. Proceed with the following steps to begin the calibration:

Proceed with the following steps to begin the calibration:

Step one: Disconnect the sampler motor from the mass flow controller and connect the motor to a stable AC power source.

Step two: Mount the calibrator orifice and top loading adapter plate to the sampler. A sampling filter is generally not used during this procedure. Tighten the top loading adapter hold down nuts securely for this procedure to assure that no air leaks are present.

Step three: Allow the sampler motor to warm up to its normal operating temperature.

Step four: Conduct a leak test by covering the hole on top of the orifice and pressure tap on the orifice with your hands. Listen for a high-pitched squealing sound made by escaping air. If this sound is heard, a leak is present and the top loading adapter hold-down nuts need to be re-tightened.

"WARNING" Avoid running the sampler for longer than 30 seconds at a time with the orifice blocked. This will reduce the chance of the motor overheating.

"WARNING" never try this leak test procedure with a manometer connected to the side tap on the calibration orifice or the blower motor. Liquid from the manometer could be drawn into the system and cause motor damage.

Step five: Connect one side of a water manometer to the pressure tap on the side of the orifice with a rubber vacuum tube. Leave the opposite side of the manometer open to the atmosphere.

Note: Both valves on the manometer have to be open for the liquid to flow freely also to read a manometer one side of the 'U' tube goes up the other goes down; add together this is the "H_2O

Step six: Turn black knob on top of calibrator **(TE-5028A)** counter clock-wise opening the four holes on the bottom wide open. Record the manometer reading from the orifice and the continuous flow recorder reading from the sampler. A manometer must be held vertically to insure accurate readings. Tapping the backside of the continuous flow recorder will help to center the pen and give accurate readings. Repeat this procedure by adjusting the knob on the orifice to five different reading. Normally the orifice reading should be between 3.0" and 4.0" of H_2O. If you are using a fixed orifice **(TE-5025A)**, five flow rates are achieved in this step by changing 5 different plates (18,13,10,7, and 5 hole plates) and taking five different readings.

Step seven: Record the ambient air temperature, the ambient barometric pressure, the sampler serial number, the orifice s/n, the orifice slope and intercept with date last certified, today's date, site location and the operator's initials.

Step eight: Disconnect the sampler motor from its power source and remove the orifice and top loading adapter plate. Re-connect the sampler motor to the electronic mass flow controller.

An example of a PM10 Sampler Calibration Data Sheet has been attached with data filled in from a typical calibration. This includes the transfer standard orifice calibration relationship which was taken from the Orifice Calibration Worksheet that accompanies the calibrator orifice. Since this calibration is for a PM10 sampler, the slope and intercept for this orifice uses **actual** flows rather than standard flows and is taken from the Qactual section of the Orifice Calibration Worksheet. The Qstandard flows are used when calibrating a TSP sampler.

The five orifice manometer readings taken during the calibration have been recorded in the column on the data worksheet titled "H_2O. The five continuous flow recorder readings taken during the calibration have been recorded under the column titled I (chart).

The orifice manometer readings need to be converted to the actual airflows they represent using the following equation:

Qa = 1/m[Sqrt((H$_2$0)(Ta/Pa))-b]

where: Qa = actual flow rate as indicated by the calibrator orifice, m^3/min
"H_20 = orifice manometer reading during calibration, (inches) "H_20

Ta = ambient temperature during calibration, K (K = 273 + °C)
Pa = ambient barometric pressure during calibration, mm Hg
m = *Qactual slope of orifice* calibration relationship
b = *Qactual intercept of orifice* calibration relationship.

Once these actual flow rates have been determined for each of the five run points, they are recorded in the column titled Qa, and are represented in cubic meters per minute.

The continuous flow recorder readings taken during the calibration need to be corrected to the current meteorological conditions using the following equation:

IC = I[Sqrt(Ta/Pa)]

where: IC = continuous flow recorder readings corrected to current Ta and Pa
I = continuous flow recorder readings during calibration
Pa = ambient barometric pressure during calibration, mm Hg.
Ta = ambient temperature during calibration, K (K = 273 + °C)

After each of the continuous flow recorder readings have been corrected, they are recorded in the column titled IC (corrected). Using Qa and IC as the x and y axis respectively, a slope, intercept, and correlation coefficient can be calculated using the least squares regression method. The correlation coefficient should never be less than 0.990 after a five point calibration. A coefficient below .990 indicates a calibration that is not linear and the calibration should be performed again. If this occurs, it is most likely the result of an air leak during the calibration.

The equations for determining the slope (m) and intercept (b) are as follows:

$$m = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}} \quad ; \quad b = \bar{y} - m\bar{x}$$

where: n = number of observations $\bar{y} = \Sigma y/n$; $\bar{x} = \Sigma x/n$ Σ = sum of

The equation for the coefficient of correlation (r) is as follows:

$$r = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sqrt{\left[\sum x^2 - \frac{\left(\sum x\right)^2}{n}\right]\left[\sum y^2 - \frac{\left(\sum y\right)^2}{n}\right]}}$$

where: n = number of observations
Σ = sum of

Example Problems

The following example problems use data from the attached calibration worksheet.

After all the sampling site information, calibrator information, and meteorological information have been recorded on the worksheet, standard air flows need to be determined from the orifice manometer readings taken during the calibration using the following equation:

1. **$Qa = 1/m[Sqrt((H_20)(Ta/Pa))-b]$**

where:
- Qa = actual flow rate as indicated by the calibrator orifice, m^3/min
- "H_20 = orifice manometer reading during calibration, (inches) "H_20
- Ta = ambient temperature during calibration, K (K = 273 + °C)
- Pa = ambient barometric pressure during calibration, mm Hg
- m = *Qactual slope of orifice* calibration relationship
- b = *Qactual intercept of orifice* calibration relationship.

Note that the ambient temperature is needed in degrees Kelvin to satisfy the Qa equation. Also, the barometric pressure needs to be reported in millimeters of mercury. In our case the two following conversions may be needed:

2. **degrees Kelvin = [5/9 (degrees Fahrenheit - 32)] + 273**

3. **millimeters of mercury = 25.4(inches of H_2O/13.6)**

Inserting the numbers from the calibration worksheet run point number one we get:

4. Qa = 1/.99486 [Sqrt((5.45)(294/753)) - (-.00899)]

5. Qa = 1.005 [Sqrt((5.45)(.390)) + .00899]

6. Qa = 1.005 [Sqrt(2.1255) + .00899]

7. Qa = 1.005[1.4579+ .00899]

8. Qa = 1.005[1.46689]

9. Qa = 1.474

Throughout these example problems you may find that your answers vary some from those arrived at here. This is probably due to different calculators carrying numbers to different decimal points. The variations are usually slight and should not be a point of concern. Also, with a good calibration there should be at least three Qa numbers in the range of 1.02 to 1.24 m^3/min (36 to 44 CFM). From the data sheet there is 4 out of 5 numbers in the range for PM10 thus a good calibration.

With the Qa determined, the corrected chart reading (IC) for this run point needs to be calculated using the following equation:

10. **IC = I[Sqrt(Ta/Pa)]**

where: IC = continuous flow recorder readings corrected to current Ta and Pa
I = continuous flow recorder readings during calibration
Pa = ambient barometric pressure during calibration, mm Hg.
Ta = ambient temperature during calibration, K (K = 273 + °C)

Inserting the data from run point one on the calibration worksheet we get:

11. IC = 56 [Sqrt(294/753)]

12. IC = 56 [Sqrt(.390)]

13. IC = 56 [.6244997]

14. IC = 34.97

This procedure should be completed for all five run points. EPA guidelines state that at least three of the five Qa flow rates during the calibration be within or nearly within the acceptable operating limits of 1.02 to 1.24 m^3/min (36 to 44 CFM). If this condition is not met, the instrument should be recalibrated.

Using Qa as our x-axis, and IC as our y-axis, a slope, intercept, and correlation coefficient can be determined using the least squares regression method.

The equations for determining the slope (m) and intercept (b) are as follows:

15. $$m = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}} \quad ; \quad b = \bar{y} - m\bar{x}$$

where: n = number of observations

$\bar{y} = \Sigma y/n$; $\bar{x} = \Sigma x/n$ Σ = sum of.

The equation for the coefficient of correlation (r) is as follows:

16. $$r = \frac{\Sigma xy - \frac{(\Sigma x)(\Sigma y)}{n}}{\sqrt{\left[\Sigma x^2 - \frac{\left(\Sigma x\right)^2}{n}\right]\left[\Sigma y^2 - \frac{\left(\Sigma y\right)^2}{n}\right]}}$$

where: n = number of observations

Σ = sum of.

Before these can be determined, some preliminary algebra is necessary. Σx, Σy, Σx^2, Σxy, $(\Sigma x)^2$,

$(\Sigma y)^2$, n, $\bar{y}$, and $\bar{x}$ need to be determined.

17. $\Sigma x = 1.475 + 1.167 + 1.115 + 1.079 + 1.060 = 5.896$
18. $\Sigma y = 35.00 + 29.37 + 28.75 + 28.12 + 27.50 = 148.74$
19. $\Sigma x^2 = (1.475)^2 + (1.167)^2 + (1.115)^2 + (1.079)^2 + (1.060)^2 = 7.069$
20. $\Sigma y^2 = (35.00)^2 + (29.37)^2 + (28.75)^2 + (28.12)^2 + (27.50)^2 = 4461.1438$
21. $\Sigma xy = (1.475)(35.00) + (1.167)(29.37) + (1.115)(28.75) + (1.079)(28.12) + (1.060)(27.50) = 177.448$
22. $n = 5$
23. $\bar{x} = \Sigma x/n = 1.1792$
24. $\bar{y} = \Sigma y/n = 29.748$
25. $(\Sigma x)^2 = (5.896)^2 = 34.763$
26. $(\Sigma y)^2 = (149.74)^2 = 22{,}123.587$

Inserting the numbers:

27. $$\text{slope} = \frac{177.448 - \frac{(5.896)(148.74)}{5}}{7.069 - \frac{34.763}{5}}$$

28. $$\text{slope} = \frac{177.448 - \frac{(876.971)}{5}}{7.069 - \frac{34.763}{5}}$$

29. $$\text{slope} = \frac{177.448 - 175.394}{7.069 - 6.953}$$

30. $$\text{slope} = \frac{2.054}{0.116}$$

31. $$\text{slope} = 17.707$$

32. $$\text{intercept} = 29.748 - (17.707)(1.1792)$$

33. $$\text{intercept} = 29.748 - 20.88$$

34. $$\text{intercept} = 8.868$$

35. $$\text{correlation coeff.} = \frac{177.448 - \frac{(5.896)(148.74)}{5}}{\sqrt{\left[7.069 - \frac{34.763}{5}\right]\left[4461.1438 - \frac{22123.587}{5}\right]}}$$

36. $$\text{correlation coeff.} = \frac{177.448 - \frac{(876.971)}{5}}{\sqrt{[(7.069 - 6.953)]\ [(4461.1438 - 4424.717)]}}$$

37. $$\text{correlation coeff.} = \frac{(177.448 - 175.394)}{\sqrt{[(7.069 - 6.953)][(4461.1438 - 4424.717)]}}$$

38. $$\text{correlation coeff.} = \frac{2.054}{\sqrt{(0.116)(36.427)}}$$

39. $$\text{correlation coeff.} = \frac{2.054}{\sqrt{4.226}}$$

40. $$\text{correlation coeff.} = \frac{2.054}{2.056}$$

41. correlation coeff. = .999

A calibration that has a correlation coefficient of less than .990 is not considered linear and should be re-calibrated. As you can see from the worksheet we have 4 Qa numbers that are in the PM10 range (1.02 - 1.24 m^3/min) and the correlation coeff. is > .990 , thus a good calibration. Next, calculate and record the SFR (sampler's seasonally adjusted set point flow rate in m^3/min).

$$SFR = 1.13 [(Ps/Pa)(Ta/Ts)]$$

where:
- SFR = sampler's seasonally adjusted set point flow rate, m^3/min
- 1.13 = designed sampling flow rate of PM10 samplers, m^3/min
- Ps = seasonal average barometric pressure, mm Hg
- Pa = actual ambient barometric pressure during calibration, mm Hg
- Ts = seasonal average temperature, K
- Ta = actual ambient temperature during calibration, K

$$SFR = 1.13 [(757/753)(294/291)]$$
$$SFR = 1.13 [(1.005312)(1.0103092)]$$
$$SFR = 1.13 [1.0156759]$$
$$SFR = 1.147 m^3/min$$

To be more accurate when using an average temperature and barometric pressure, it is better to use a daily, weekly, or monthly average instead of a seasonal average.

Then, calculate and record the SSP, sampler's seasonally adjusted recorder set point.

$$SSP = [m * SFR + b] [Sqrt(Pa/Ta)]$$

where:
- SSP = sampler's recorder set point, recorder response
- m = slope of sampler from linear regression
- SFR = sampler's seasonally adjusted set point flow rate, m^3/min

b = intercept of sampler from linear regression

Sqrt = square root

Pa = actual ambient barometric pressure during calibration, mm Hg

Ta = actual ambient temperature during calibration, K

SSP = [17.6685 * 1.147 + 8.9094] [Sqrt(753/294)]

SSP = [29.175169] [Sqrt(2.5612244)]

SSP = [29.175169] [1.6003825]

SSP = 46.69

The SSP is the design operating flow rate of the PM10 High Volume Sampler, 1.13 m^3/min or 40 CFM, corrected to the current ambient temperature and barometric pressure. Adjust the mass flow controller to agree with the above determined SSP. This is done by loading the sampler with a piece of Micro-Quartz filter. Turn on the sampler and allow it to warm up to normal operating conditions. Adjust the mass flow controller set screw (turning pot) until the flow/pressure recorder reads 46.69. The sampler should now be sampling at the designed flow rate of 1.13 m^3/min or 40 CFM, corrected to current meteorological conditions.

Tisch Environmental, Inc.
PM10 High Volume Sampler Calibration

SITE

Location-> Cleves, Ohio Date-> 1-2000
Sampler-> TE-6070BL, TE-6070D-BL Tech-> Jim Tisch

CONDITIONS

Sampler Elevation (feet)	400		
Sea Level Pressure (in Hg)	30.05	Corrected Pressure (mm Hg)	753
Temperature (deg F)	70	Temperature (deg K)	294
Seasonal SL Press. (in Hg)	30.20	Corrected Seasonal (mm Hg)	757
Seasonal Temp. (deg F)	65	Seasonal Temp. (deg K)	291

CALIBRATION ORIFICE

Make-> Tisch Environmental, Inc Slope-> 0.99486
Model-> TE-5025A Intercept-> -0.00899
Serial#-> 3 Date Certified-> Original

Plate or Test #	H2O (in)	CALIBRATION Qa (m3/min)	I (chart)	IC (corrected)	LINEAR REGRESSION
1	5.45	1.475	56.0	35.00	Slope = 17.6683
2	3.40	1.167	47.0	29.37	Intercept = 8.9094
3	3.10	1.115	46.0	28.75	Corr. coeff.= 0.9988
4	2.90	1.079	45.0	28.12	SFR = 1.147
5	2.80	1.060	44.0	27.50	SSP = 46.67

CALCULATIONS

Qa = 1/m(Sqrt((H2O)(Ta/Pa))-b)
IC = I(Sqrt(Ta/Pa))

Qa = actual flow rate
IC = corrected chart response
m = calibrator slope
b = calibrator intercept
Ta = actual temperature (deg K)
Pa = actual pressure (mm Hg)

SFR = 1.11(Ps/Pa)(Ta/Ts)
SSP = (m*SFR+b)(Sqrt(Pa/Ta))

SFR = sampler set point flow rate
SSP = sampler chart set point
m = sampler slope
b = sampler intercept
Ta = actual temperature (deg K)
Pa = actual pressure (mm Hg)
Ts = seasonal temperature (deg K)
Ps = seasonal pressure (mm Hg)

For subsequent calculation of sampler flow:
1/m((I)(Sqrt(Tav/Pav))-b)

m = sampler slope
b = sampler intercept
I = chart response
Tav = daily average temperature
Pav = daily average pressure

CALIBRATION PROCEDURE for TE-6070-BL, TE-6070D-BL

The following is a step-by-step process of the calibration of a **TE-6070-BL, TE-6070D-BL Brush-less Mass Flow Controlled PM10 High Volume Sampling Systems.** Following these steps are example calculations determining the calibration flow rates, and resulting slope and intercept for the sampler. These instructions pertain to the samplers that have flow controlled by electronic mass flow controllers (MFC) in conjunction with a continuous flow recorder. This calibration differs from that of a volumetric flow controlled sampler. The attached example calibration worksheets can be used with either a **TE-5025 Fixed Orifice Calibrator** that utilizes resistance plates to simulate airflow or a **TE-5028 Variable Orifice Calibrator** that uses an adjustable or variable orifice. The attached worksheet uses a variable orifice. Either type of orifice is acceptable for calibrating high volume samplers the calibration process remains the same. Proceed with the following steps to begin the calibration:

Step one: Mount the calibrator orifice and top loading adapter plate to the sampler. A sampling filter is generally not used during this procedure. Tighten the top loading adaptor. Hold down nuts securely for this procedure to ensure that no air leaks are present.

Step two: Disconnect brush-less motor for the brush-less mass flow controller (Squeeze 5 wire plug together and pull apart).

Step three: Connect the "Brushless MFC Calibration By-pass Adapter" to the brush-less motor.

Step four: Connect a fresh 9-volt battery to the battery clip of the Adapter. When you plug mail cord on Adapter into the source voltage, the brush-less motor will now operate at full speed during the calibration procedure until Adapter is disconnected or the 9-volt battery is disconnected.

Step five: Plug Adapter into the source voltage.

Step six: Allow the sampler motor to warm up to its normal operating temperature.

Step seven: Conduct a leak test by covering the hole on top of the orifice and pressure tap on the orifice with your hands. Listen for a high-pitched squealing sound made by escaping air. If this sound is heard, a leak is present and the top loading adapter hold-down nuts need to be re-tightened.

"WARNING" Avoid running the sampler for longer than 30 seconds at a time with the orifice

blocked. This will reduce the chance of the motor overheating.

"WARNING" never try this leak test procedure with a manometer connected to the side tap on the calibration orifice or the blower motor. Liquid from the manometer could be drawn into the system and cause motor damage.

Step eight: Connect one side of a water manometer to the pressure tap on the side of the orifice with a rubber vacuum tube. Leave the opposite side of the manometer open to the atmosphere. Both valves on the manometer have to be open for the liquid to flow freely. Also, to read a manometer, one side of the 'U' tube goes up and the other goes down; added together this is the "H_2O

Step nine: Turn black knob on top of calibrator **(TE-5028A)** counter clock-wise opening the four holes on the bottom wide open. Record the manometer reading from the orifice and the continuous flow recorder reading from the sampler. A manometer must be held vertically to insure accurate readings. Tapping the backside of the continuous flow recorder will help to center the pen and give accurate readings. Repeat this procedure by adjusting the knob on the orifice to five different reading. Normally the orifice reading should be between 3.0" and 4.0" of H_2O. If you are using a fixed orifice **(TE-5025A)**, five flow rates are achieved in this step by changing 5 different plates (18,13,10,7, and 5 hole plates) and taking five different readings.

Step ten: Record the ambient air temperature, the ambient barometric pressure, the sampler serial number, the orifice s/n, the orifice slope and intercept with date last certified, today's date, site location and the operator's initials.

Step eleven: Unplug the Adapter from the source voltage (the motor will shut off), unplug the battery, and reconnect the brush-less motor to the brush-less mass flow controller.

Step twelve: Remove the orifice and top-loading adapter plate.

An example of a PM10 Sampler Calibration Data Sheet has been attached with data filled in from a typical calibration. This includes the transfer standard orifice calibration relationship which was taken from the Orifice Calibration Worksheet that accompanies the calibrator orifice. Since this calibration is for a PM10 sampler, the slope and intercept for this orifice uses **actual** flows rather than standard flows and is taken from the Qactual section of the Orifice Calibration Worksheet. The Qstandard flows are used when calibrating a TSP sampler.

The five orifice manometer readings taken during the calibration have been recorded in the column on the data worksheet titled "H_2O. The five continuous flow recorder readings taken during the

calibration have been recorded under the column titled I (chart).

The orifice manometer readings need to be converted to the actual airflows they represent using the following equation:

Qa = 1/m[Sqrt((H20)(Ta/Pa))-b]

where: Qa = actual flow rate as indicated by the calibrator orifice, m^3/min
"H20 = orifice manometer reading during calibration, (inches) "H20

Ta = ambient temperature during calibration, K (K = 273 + °C)
Pa = ambient barometric pressure during calibration, mm Hg
m = *Qactual slope of orifice* calibration relationship
b = *Qactual intercept of orifice* calibration relationship.

Once these actual flow rates have been determined for each of the five run points, they are recorded in the column titled Qa, and are represented in cubic meters per minute.

The continuous flow recorder readings taken during the calibration need to be corrected to the current meteorological conditions using the following equation:

IC = I[Sqrt(Ta/Pa)]

where: IC = continuous flow recorder readings corrected to current Ta and Pa
I = continuous flow recorder readings during calibration
Pa = ambient barometric pressure during calibration, mm Hg.
Ta = ambient temperature during calibration, K (K = 273 + °C)

After each of the continuous flow recorder readings have been corrected, they are recorded in the column titled IC (corrected).

Using Qa and IC as the x and y axis respectively, a slope, intercept, and correlation coefficient can be calculated using the least squares regression method. The correlation coefficient should never be less than 0.990 after a five point calibration. A coefficient below .990 indicates a calibration that is not linear and the calibration should be performed again. If this occurs, it is most likely the result of an air leak during the calibration.

The equations for determining the slope (m) and intercept (b) are as follows:

$$m = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}} \quad ; \quad b = \bar{y} - m\bar{x}$$

where: n = number of observations $\bar{y} = \Sigma y/n$; $\bar{x} = \Sigma x/n$ Σ = sum of

The equation for the coefficient of correlation (r) is as follows:

$$r = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sqrt{\left[\sum x^2 - \frac{\left(\sum x\right)^2}{n}\right]\left[\sum y^2 - \frac{\left(\sum y\right)^2}{n}\right]}}$$

where: n = number of observations
Σ = sum of

Example Problems

The following example problems use data from the attached calibration worksheet.

After all the sampling site information, calibrator information, and meteorological information have been recorded on the worksheet, standard air flows need to be determined from the orifice manometer readings taken during the calibration using the following equation:

1. **Qa = 1/m[Sqrt((“H_20)(Ta/Pa))-b]**

where: Qa = actual flow rate as indicated by the calibrator orifice, m^3/min
“H_20 = orifice manometer reading during calibration, (inches) “H_20
Ta = ambient temperature during calibration, K (K = 273 + °C)
Pa = ambient barometric pressure during calibration, mm Hg
m = *Qactual slope of orifice* calibration relationship
b = *Qactual intercept of orifice* calibration relationship.

Note that the ambient temperature is needed in degrees Kelvin to satisfy the Qa equation. Also, the barometric pressure needs to be reported in millimeters of mercury. In our case the two following conversions may be needed:

2. **degrees Kelvin = [5/9 (degrees Fahrenheit - 32)] + 273**

3. **millimeters of mercury = 25.4(inches of H_2O/13.6)**

Inserting the numbers from the calibration worksheet run point number one we get:

4. Qa = 1/.99486 [Sqrt((5.45)(294/753)) - (-.00899)]
5. Qa = 1.005 [Sqrt((5.45)(.390)) + .00899]
6. Qa = 1.005 [Sqrt(2.1255) + .00899]
7. Qa = 1.005[1.4579+ .00899]
8. Qa = 1.005[1.46689]
9. Qa = 1.474

Throughout these example problems you may find that your answers vary some from those arrived at here. This is probably due to different calculators carrying numbers to different decimal points. The variations are usually slight and should not be a point of concern. Also, with a good calibration there should be at least three Qa numbers in the range of 1.02 to 1.24 m^3/min (36 to 44 CFM). From the data sheet there is 4 out of 5 numbers in the range for PM10 thus a good calibration.

With the Qa determined, the corrected chart reading (IC) for this run point needs to be calculated using the following equation:

10. **IC = I[Sqrt(Ta/Pa)]**

where: IC = continuous flow recorder readings corrected to current Ta and Pa
I = continuous flow recorder readings during calibration
Pa = ambient barometric pressure during calibration, mm Hg.
Ta = ambient temperature during calibration, K (K = 273 + °C)

Inserting the data from run point one on the calibration worksheet we get:

11. IC = 56 [Sqrt(294/753)]
12. IC = 56 [Sqrt(.390)]
13. IC = 56 [.6244997]
14. IC = 34.97

This procedure should be completed for all five run points. EPA guidelines state that at least three of the five Qa flow rates during the calibration be within or nearly within the acceptable operating limits of 1.02 to 1.24 m^3/min (36 to 44 CFM). If this condition is not met, the instrument should be recalibrated.

Using Qa as our x-axis, and IC as our y-axis, a slope, intercept, and correlation coefficient can be determined using the least squares regression method.

The equations for determining the slope (m) and intercept (b) are as follows:

15. $$m = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}} \quad ; \quad b = \bar{y} - m\bar{x}$$

where: n = number of observations

$\bar{y} = \Sigma y/n$; $\bar{x} = \Sigma x/n$ Σ = sum of.

The equation for the coefficient of correlation (r) is as follows:

16. $$r = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sqrt{\left[\sum x^2 - \frac{\left(\sum x\right)^2}{n}\right]\left[\sum y^2 - \frac{\left(\sum y\right)^2}{n}\right]}}$$

where: n = number of observations

Σ = sum of.

Before these can be determined, some preliminary algebra is necessary. Σx, Σy, Σx^2, Σxy, $(\Sigma x)^2$, $(\Sigma y)^2$, n, $\bar{y}$, and $\bar{x}$ need to be determined.

17. $\Sigma x = 1.475 + 1.167 + 1.115 + 1.079 + 1.060 = 5.896$
18. $\Sigma y = 35.00 + 29.37 + 28.75 + 28.12 + 27.50 = 148.74$
19. $\Sigma x^2 = (1.475)^2 + (1.167)^2 + (1.115)^2 + (1.079)^2 + (1.060)^2 = 7.069$
20. $\Sigma y^2 = (35.00)^2 + (29.37)^2 + (28.75)^2 + (28.12)^2 + (27.50)^2 = 4461.1438$
21. $\Sigma xy = (1.475)(35.00) + (1.167)(29.37) + (1.115)(28.75) + (1.079)(28.12) + (1.060)(27.50) = 177.448$
22. $n = 5$
23. $\bar{x} = \Sigma x/n = 1.1792$
24. $\bar{y} = \Sigma y/n = 29.748$
25. $(\Sigma x)^2 = (5.896)^2 = 34.763$
26. $(\Sigma y)^2 = (149.74)^2 = 22{,}123.587$

Inserting the numbers:

27. $$\text{slope} = \frac{177.448 - \frac{(5.896)(148.74)}{5}}{34.763}$$

$$7.069 - 5$$

29. $$\text{slope} = \frac{177.448 - \frac{(876.971)}{5}}{7.069 - \frac{34.763}{5}}$$

29. $$\text{slope} = \frac{177.448 - 175.394}{7.069 - 6.953}$$

30. $$\text{slope} = \frac{2.054}{0.116}$$

31. $$\text{slope} = 17.707$$

32. $$\text{intercept} = 29.748 - (17.707)(1.1792)$$

33. $$\text{intercept} = 29.748 - 20.88$$

34. $$\text{intercept} = 8.868$$

35. $$\text{correlation coeff.} = \frac{177.448 - \frac{(5.896)(148.74)}{5}}{\sqrt{\left[7.069 - \frac{34.763}{5}\right]\left[4461.1438 - \frac{22123.587}{5}\right]}}$$

36. $$\text{correlation coeff.} = \frac{177.448 - \frac{(876.971)}{5}}{\sqrt{[(7.069 - 6.953)]\ [(4461.1438 - 4424.717)]}}$$

37. $$\text{correlation coeff.} = \frac{(177.448 - 175.394)}{\sqrt{[(7.069 - 6.953)][(4461.1438 - 4424.717)]}}$$

38. $$\text{correlation coeff.} = \frac{2.054}{\sqrt{(0.116)(36.427)}}$$

39. $$\text{correlation coeff.} = \frac{2.054}{\sqrt{4.226}}$$

40. correlation coeff. = $\frac{2.054}{2.056}$

41. correlation coeff. = .999

A calibration that has a correlation coefficient of less than .990 is not considered linear and should be re-calibrated. As you can see from the worksheet we have 4 Qa numbers that are in the PM10 range (1.02 - 1.24 m^3/min) and the correlation coeff. is > .990 , thus a good calibration.

Next, calculate and record the SFR (sampler's seasonally adjusted set point flow rate in m^3/min).

$$SFR = 1.13 [(Ps/Pa)(Ta/Ts)]$$

where:
- SFR = sampler's seasonally adjusted set point flow rate, m^3/min
- 1.14 = designed sampling flow rate of PM10 samplers, m^3/min
- Ps = seasonal average barometric pressure, mm Hg
- Pa = actual ambient barometric pressure during calibration, mm Hg
- Ts = seasonal average temperature, K
- Ta = actual ambient temperature during calibration, K

SFR = 1.13 [(757/753)(294/291)]
SFR = 1.13 [(1.005312)(1.0103092)]
SFR = 1.13 [1.0156759]
SFR = 1.147 m^3/min

To be more accurate when using an average temperature and barometric pressure, it is better to use a daily, weekly, or monthly average instead of a seasonal average.

Then, calculate and record the SSP, sampler's seasonally adjusted recorder set point.

$$SSP = [m * SFR + b] [Sqrt(Pa/Ta)]$$

where:
- SSP = sampler's recorder set point, recorder response

m = slope of sampler from linear regression

SFR = sampler's seasonally adjusted set point flow rate, m^3/min

b = intercept of sampler from linear regression

Sqrt = square root

Pa = actual ambient barometric pressure during calibration, mm Hg

Ta = actual ambient temperature during calibration, K

SSP = [17.6685 * 1.147 + 8.9094] [Sqrt(753/294)]

SSP = [29.175169] [Sqrt(2.5612244)]

SSP = [29.175169] [1.6003825]

SSP = 46.69

The SSP is the design operating flow rate of the PM10 High Volume Sampler, 1.13 m^3/min or 40 CFM, corrected to the current ambient temperature and barometric pressure. Adjust the mass flow controller to agree with the above determined SSP. This is done by loading the sampler with a piece of Micro-Quartz filter. Turn on the sampler and allow it to warm up to normal operating conditions. Adjust the mass flow controller set screw (turning pot) until the flow/pressure recorder reads 46.69. The sampler should now be sampling at the designed flow rate of 1.13 m^3/min or 40 CFM, corrected to current meteorological conditions.

Tisch Environmental, Inc.
PM10 High Volume Sampler Calibration

SITE

Location-> Cleves, Ohio — Date-> 1-2000
Sampler-> TE-6070BL, TE-6070D-BL — Tech-> Jim Tisch

CONDITIONS

Sampler Elevation (feet)	400		
Sea Level Pressure (in Hg)	30.05	Corrected Pressure (mm Hg)	751
Temperature (deg F)	70	Temperature (deg K)	294
Seasonal SL Press. (in Hg)	30.20	Corrected Seasonal (mm Hg)	767
Seasonal Temp. (deg F)	65	Seasonal Temp. (deg K)	291

CALIBRATION ORIFICE

Make-> Tisch Environmental, Inc — Slope-> 0.99486
Model-> TE-5025A — Intercept-> -0.00859
Serial#-> 3 — Date Certified-> Original

Plate or Test #	H2O (in)	Qa (m3/min)	I (chart)	IC (corrected)	LINEAR REGRESSION
1	5.45	1.475	56.0	35.00	Slope = 17.6685
2	3.40	1.167	47.0	29.37	Intercept = 6.9094
3	3.10	1.115	46.0	28.75	Corr. coeff.= 0.9988
4	2.90	1.079	45.0	28.12	SFR = 1.147
5	2.80	1.060	44.0	27.50	SSP = 46.67

CALCULATIONS

$Qa = 1/m(Sqrt((H2O)(Ta/Pa))-b)$
$IC = I(Sqrt(Ta/Pa))$

Qa = actual flow rate
IC = corrected chart response
m = calibrator slope
b = calibrator intercept
Ta = actual temperature (deg K)
Pa = actual pressure (mm Hg)

$SFR = 1.13(Ps/Pa)(Ta/Ts)$
$SSP = (m*SFR+b)(Sqrt(Pa/Ta))$

SFR = sampler set point flow rate
SSP = sampler chart set point
m = sampler slope
b = sampler intercept
Ta = actual temperature (deg K)
Pa = actual pressure (mm Hg)
Ts = seasonal temperature (deg K)
Ps = seasonal pressure (mm Hg)

For subsequent calculation of sampler flow:
$1/m((I)(Sqrt(Tav/Pav))-b)$

m = sampler slope
b = sampler intercept
I = chart response
Tav = daily average temperature
Pav = daily average pressure

CALIBRATION PROCEDURE for TE-6070V, TE-6070DV, TE-6070V-BL, TE-6070DV-BL

The following is a step by step process of the calibration of a **TE-6070V, TE-6070DV, TE-6070V-BL, TE-6070DV-BL Volumetric Flow Controlled PM10 Particulate Sampling System.** Following these steps are example calculations determining the calibration flow rates for the sampler. The flow rate of the sampling system is controlled by a Volumetric Flow Controller (VFC) or dimensional venturi device. This calibration differs from that of a mass flow controlled PM10 sampler in that a slope and intercept does not have to be calculated to determine air flows. The flows are converted from actual to standard conditions when the particulate concentrations are calculated. With a **V**olumetric **F**low **C**ontrolled (VFC) sampler, the calibration flow rates are provided in a **Flow Look Up Table** that accompanies each sampler. The attached example calibration worksheet uses a TE-5028A **Variable Orifice Calibrator** that uses an adjustable or variable orifice, which we recommend when calibrating a **VFC**.

Proceed with the following steps to begin the calibration.

Step one: Mount the calibrator orifice and top loading adapter plate to the sampler. A sampling filter is generally not used during this procedure. Tighten the top loading adapter hold down nuts securely for this procedure to assure that no air leaks are present.

Step two: Turn on the sampler and allow it to warm up to its normal operating temperature.

Step three: Conduct a leak test by covering the holes on top of the orifice and pressure tap on the orifice with your hands. Listen for a high-pitched squealing sound made by escaping air. If this sound is heard, a leak is present and the top loading adapter hold-down nuts need to be re-tightened.

"WARNING" Avoid running the sampler for longer than 30 seconds at a time with the orifice blocked. This will reduce the chance of the motor overheating.

"WARNING" never try this leak test procedure with a manometer connected to the side tap on the calibration orifice or the blower motor. Liquid from the manometer could be drawn into the system and cause motor damage.

Step four: Connect one side of a water manometer or other type of flow measurement device to the pressure tap on the side of the orifice with a rubber vacuum tube. Leave the opposite side of the manometer open to the atmosphere

Step five: Connect a water manometer to the quick disconnect located on the side of the aluminum outdoor shelter (this quick disconnect is connected to the pressure tap on the side of the filter

holder). If using the **TE-5025A (**a fixed orifice that uses load plates) orifice a longer manometer >30" is used here as there is a possibility of great pressure difference from this port.

Step six: Make sure the TE-5028A orifice is all the way open (turn the black knob counter clock-wise). Record both manometer readings the one from the orifice and the other from the side of the sampler. To read a manometer one side goes up and the other side goes down you add both sides, this is your inches of water. Repeat this process for the other four points by adjusting
the knob on the variable orifice (just a slight turn) to four different positions and taking four different readings. You should have five sets of numbers, ten numbers in all.

Step seven: Remove the variable orifice and the top loading adapter and install a clean Micro-Quartz filter. Record the manometer reading from the side tap on the side of the sampler. This is used to calculate the operational flow rate of the sampler.

Step eight: Record the ambient air temperature, the ambient barometric pressure, the sampler serial number, the orifice serial number, the orifice Qactual slope and intercept with date last certified, today's date, site location and the operators initials.

An example of a Volumetric Flow Controlled Sampler Calibration Data Sheet has been attached with data filled in from a typical calibration. This includes the transfer standard orifice calibration relationship which was taken from the Orifice Calibration Worksheet that accompanies the calibrator orifice. The slope and intercept are taken from the **Qactual** section of the Orifice Calibration Worksheet.

The five orifice manometer readings taken during the calibration have been recorded in the column on the calibration worksheet titled Orifice H_2O. The five manometer readings taken from the side pressure tap have been recorded in the column titled Sampler "Hg.

The first step is to convert the orifice readings to the amount of actual air flow they represent using the following equation:

$$\mathbf{Qa = 1/m[Sqrt((H_2O)(Ta/Pa))-b]}$$

where: Qa = actual flow rate as indicated by the calibrator orifice, m^3/min
"H_2O = orifice manometer reading during calibration, in. "H_2O
Ta = ambient temperature during calibration, K (K = 273 + °C)
Pa = ambient barometric pressure during calibration, mm Hg
m = slope of *Q actual* orifice calibration relationship

b = intercept of *Q actual* orifice calibration relationship.

Once these actual flow rates have been determined for each of the five run points, they are recorded in the column titled Qa, and are represented in cubic meters per minute. EPA guidelines state that at least three of these calibrator flow rates should be between 1.02 to 1.24 m^3/min (36 to 44 CFM). This is the acceptable operating flow rate range of the sampler. If this condition is not met, the sampler should be recalibrated. An air leak in the calibration system may be the source of this problem. In some cases, a filter may have to be in place during the calibration to meet this condition.

The sampler H_2O readings need to be converted to mm Hg and recorded in the column titled Pf. This is done using the following equation:

$Pf = 25.4 (in.\ H_2O/13.6)$

where: Pf is recorded in mm Hg
in. H_2O = sampler side pressure reading during calibration.

Po/Pa is calculated next. This is used to locate the sampler calibration air flows found in the Look Up Table. This is done using the following equation:

$Po/Pa = 1 - Pf/Pa$

where: Pa = ambient barometric pressure during calibration, mm Hg.

Using Po/Pa and the ambient temperature during the calibration, consult the Look Up Table to find the actual flow rate. Record these flows in the column titled Look Up.

Calculate the percent difference between the calibrator flow rates and the sampler flow rates using the following equation:

% Diff. = (Look Up Flow - Qa)/Qa * 100

where: Look Up Flow = Flow found in Look Up Table, m^3/min
Qa = orifice flow during calibration, m^3/min.

The EPA guidelines state that the percent difference should be within + or - 3 or 4%. If they are greater than this a leak may have been present during calibration and the sampler should be recalibrated.

Operational Flow Rate

Operational Flow Rate is the flow rate at which the VFC sampler is actually operating at. The line on the worksheet labeled Operational Flow Rate is where the side tap reading is recorded which is taken with only a clean filter in place. With this side tap reading, Pf and Po/Pa are calculated with the same equations listed above. This reading should be between 1.02 to 1.24 m^3/min (36 to 44 CFM), the acceptable operating range.

This completes the calibration of this sampler.

Example Problems

The following example problems use data from the attached VFC sampler calibration worksheet.
After all the sampling site information, calibrator information, and meteorological information have been recorded on the worksheet, actual air flows need to be determined from the orifice manometer readings taken during the calibration using the following equation:

1. **$Qa = 1/m[Sqrt((H_2O)(Ta/Pa))-b]$** Where:
2. Qa = actual flow rate as indicated by the calibrator orifice, m^3/min
3. " H_2O = orifice manometer reading during calibration, in. "H_2O
4. Ta = ambient temperature during calibration, K (K = 273 + °C)
5. Pa = ambient barometric pressure during calibration, mm Hg
6. m = slope of *Q actual* orifice calibration relationship
7. b = intercept of *Q actual* orifice calibration relationship.

Note that the ambient temperature is needed in degrees Kelvin to satisfy the Qa equation. Also, the barometric pressure needs to be reported in millimeters of mercury (if sea level barometric pressure is used it must be corrected to the site elevation). In our case the two following conversions may be needed:

8. **degrees Kelvin = [5/9 (degrees Fahrenheit - 32)] + 273**
9. **millimeters of mercury = 25.4(inches of H_2O/13.6)**

Inserting the numbers from the calibration worksheet test number one we get:

10. Qa = 1/.99[Sqrt((3.2)(295/747))- (- 0.02866)]
11. Qa = 1.01[Sqrt((3.2)(.3949129)) – (- 0.02866)]
12. Qa = 1.01[Sqrt(1.2637212) – (- 0.02866)]
13. Qa = 1.01[1.1241535 – (- 0.02866)]
14. Qa = 1.01[1.1528135]
15. Qa = 1.164

It is possible that your answers to the above calculations may vary. This is most likely due to different calculators carrying numbers to different decimal points. This should not be an area of concern as generally these variations are slight.

With Qa determined, the sampler H_2O reading needs to be converted to mm Hg using the following equation:

16. **Pf = 25.4 (in. H_2O/13.6)** where:
17. Pf is recorded in mm Hg
18. in. H_2O = sampler side pressure reading during calibration

Inserting the numbers from the worksheet:

19. Pf = 25.4(17.3/13.6)
20. Pf = 25.4(1.2720588)
21. Pf = 32.31 mm Hg

Po/Pa is calculated next. This is done using the following equation:

22. **Po/Pa = 1 - Pf/Pa**
23. where: Pa = ambient barometric pressure during calibration, mm Hg.

Inserting the numbers from the worksheet:

24. Po/Pa = 1 – 32.31/747
25. Po/Pa = 1- .0167989
26. Po/Pa = .957

Use Po/Pa and the ambient temperature during the calibration (Ta) to locate the flow for the calibration point in the Look Up table. Record this in the column titled Look Up. Calculate the percent difference using the following equation:

27. **% Difference = (Look Up flow - Qa)/Qa * 100**

Inserting the numbers from the worksheet:

28. % Difference = (1.193 - 1.164)/1.164 * 100

29. % Difference = (0.029)/1.164 * 100

30. % Difference = (0.024914) * 100

31. % Difference = 2.49

The above calculations have to be performed for all five calibration points.

Operational Flow Rate

Take a side tap reading with only a filter in place.

in. H_2O = 21.75

1. **Pf = 25.4 (in. H_2O/13.6)** where:

2. Pf is recorded in mm Hg

3. in. H_2O = sampler side pressure reading with filter in place

4. Pf = 25.4(21.75/13.6)

5. Pf = 25.4(1.5992647)

6. Pf = 40.62 mm Hg

Po/Pa is calculated next. This is done using the following equation:

7. **Po/Pa = 1 - Pf/Pa**

8. where: Pa = ambient barometric pressure during calibration, mm Hg.

Inserting the numbers from the worksheet:

9. Po/Pa = 1 – 40.62/747

10. Po/Pa = 1- .0543775

11. Po/Pa = .946

Use Po/Pa and the ambient temperature during the calibration (Ta) to locate the flow for the calibration point in the Look Up table.

Po/Pa = .946 Ta = 22 Look up table reading = 1.178 m^3/min

This reading should be between 1.02 to 1.24 m^3/min (36 to 44 CFM), the acceptable operating range. Record this in the column titled Look Up.

Calculate the percent difference using the following equation:

12. **% Difference = (Look Up flow - 1.13)/1.13 * 100**

13. % Difference = (1.178 - 1.13)/1.113 * 100

14. % Difference = (0.048)/1.13 * 100

15. % Difference = (0.0424778) * 100

16. % Difference = 4.24778

In this case the % Difference has to be + or - 10% of 1.13 or 40 CFM which is 1.02 to 1.24 m^3/min or 36 to 44 CFM, the acceptable operating range.

Tisch Environmental, Inc.
Particulate Sampler Calibration
Volumetric Flow Controller

Site		Calibration Orifice	
Location-->	Cleves, Ohio	Make--->	28A
Date------>	11-98	Model-->	Tisch TE-5
Tech.----->	Jim Tisch	Serial->	88
Sampler--->	TE-6070V, DV, V-BL, DV-BL	Slope-->	0.99000
Serial#--->	P4900 PM10	Int.--->	-0.02866

Temperature (deg F)	71	Elevation (ft)	500
Ta (deg K)	295	SL Press (in Hg)	29.92
Ta (deg C)	22	Pa (mm Hg)	747

Plate #	Orifice "H2O	Qa m3/min	Sampler "Hg	Pf mm Hg	Po/Pa	Look Up m3/min	% Diff
1	3.20	1.164	1.27	32.26	0.957	1.193	2.50
2	3.15	1.155	1.40	35.56	0.952	1.186	2.69
3	3.10	1.146	1.45	36.83	0.951	1.185	3.40
4	3.10	1.146	1.55	39.37	0.947	1.180	2.97
5	3.00	1.128	2.20	55.88	0.925	1.150	1.97
OPERATIONAL FLOW RATE			1.60	40.64	0.946	1.178	4.25

Calculations

Calibrator Flow (Qa) = 1/Slope*(SQRT(H20*(Ta/Pa))-Intercept)

Pressure Ratio (Po/Pa) = 1-Pf/Pa

% Difference = (Look Up Flow-Calibrator Flow)/Calibrator Flow*100

TOTAL VOLUME CALCULATIONS for Mass Flow Controlled PM10 Systems

TE-6070, TE-6070D, TE-6070BL, TE-6070D-BL

To calculate the total volume of air sampled through the (filter) during your sampling run, take a set-up reading (when you set the sampler up the SSP was 46.69, which is set up reading) and an ending reading, look at recorder chart and use the number where red ink pen stops, goes down, for our example lets assume the ending number was 45. Take 46.69 + 45 = 91.69 91.69/2 = 45.85. So the continuous recorder reading you would use is 45.85. Put that into formula on bottom of worksheet.

1/m((I)[Sqrt(Tav/Pav)]- b)

m = sampler slope
b = sampler intercept
I = average chart response
Tav = daily, weekly, monthly, or seasonal average temperature
Pav = daily, weekly, monthly, or seasonal average barometric pressure
Sqrt = square root

Example:

m^3/min = 1/17.6685((45.85)[Sqrt(291/757)]-(8.9094))
m^3/min = .0566 ((45.85)[Sqrt(.3844)] – 8.9094)
m^3/min = .0566 ((45.85)[.62] - 8.9094)
m^3/min = .0566 ((28.427) – 8.9094)
m^3/min = .0566 (19.5176)
m^3/min = 1.105
ft^3/min = 1.105 x 35.31 = 39.01
Total ft^3 = ft^3/min x 60 x hours that sampler ran

Assume our sampler ran 23.8 hours (end ETI reading - start ETI reading)

** Be certain ETI is in hours otherwise convert to hours **

Total ft^3 = 39.01 x 60 x 23.8 = 55,706.28 ft^3

Total m^3 = 1.105 x 60 x 23.8 = 1577.94 m^3

"Note" Reference page 66 see Appendix J for Filter Handling, Conditioning, Weighing, and Calculation of PM10 Concentration Measurements.

Total Volume Calculations for Volumetric Flow Controlled Systems

TE-6070V, TE-6070DV, TE-6070V-BL, TE-6070DV-BL

USE OF LOOK-UP-TABLE FOR DETERMINATION OF FLOW RATE

(NOTE: Individual Look Up Tables will vary.)

1. Suppose the ambient conditions are:
   Temperature: $T_a = 24\,^oC$
   Barometric Pressure: P_a = 762 mm Hg (this must be station pressure which is not corrected to sea level)
2. Assume system is allowed to warm up for stable operation.
3. Measure filter pressure differential, P_f. This reading is the set-up reading plus pick-up reading divided by 2 for an average reading. This is taken with a differential manometer with one side of the manometer connected to the stagnation tap on the filter holder (or the Bulkhead Fitting) and the other side open to the atmosphere. Filter must be in place during this measurement.

Assume that:

Set-up Reading: $P_f = 21.75$ in H_2O
Pick-up Reading: $P_f = 22.5$ in H_2O

$P_f = (21.75 + 22.5)/2 = 22.125$ in H_2O.

4. Convert P_f = to same units as barometric pressure.
   $P_f = 22.125$ in H_2O / 13.61 x 25.4 = 41.29 mm Hg
   $P_f = 41.29$ mm Hg

5. Calculate pressure ratio.
   $P_o/P_a = 1 - (P_f/P_a)$

NOTE: P_f and P_a MUST HAVE CONSISTENT UNITS

$P_o/P_a = 1 - (41.29 / 762)$
$P_o/P_a = .946$

6. Look up Flow Rate from table.
   Table 1 is set up with temperature in ^oC and the Flow Rate is read in units of m^3/min (actual, ACMM). In table 2 the temperature is in ^oF and Flow Rate is read in ft^3/min (actual, ACFM).

   a) For the example we will use Table 1.
   Locate the temperature and pressure ratio entries nearest the conditions of:

$T_a = 24^oC$
$P_o/P_a = .946$

Example: Look-Up Table for Actual Flow Rate in Units of m^3/min

Temperature ^{o}C

Po/Pa	22	24	26	28	30
0.944	1.176	1.179	1.183	1.186	1.190
0.945	1.177	1.181	1.184	1.188	1.191
0.946	1.178	1.182	1.186	1.189	1.193
0.947	1.180	1.183	1.187	1.190	1.194
0.948	1.181	1.185	1.188	1.192	1.195
0.949	1.182	1.186	1.190	1.193	1.197

b) The reading of flow rate is:
Q_a = 1.182 m^3/min (actual)

If your Po/Pa number is not in look up table ie; >.979 then interpolate.

7. Determine flow rate in terms of standard air.

$$Q_{std} = 1.182\ m^3/\min \left(\frac{762\ mm\ Hg}{760\ mm\ Hg}\right)\left(\frac{298K}{(273+24)\,K}\right)$$

Q_{std} = 1.189 std m^3/min

Total Volume

Assume our sampler ran 23.8 hours (end ETI reading - start ETI reading)

** Make sure ETI is in hours otherwise convert to hours **

actual Total m^3 = 1.182 x 60 x 23.8 = 1687.9 m^3
standard Total m^3 = 1.189 x 60 x 23.8 = 1697.9 m^3

To convert to cubic feet multiply m^3 by 35.31

"Note" Reference page 66 see Appendix J for Filter Handling, Conditioning, Weighing, and Calculation of PM10 Concentration Measurements.

SAMPLER OPERATION

TE-6070, TE-6070D, TE-6070BL, TE-6070D-BL, TE-6070V, TE-6070DV, TE-6070V-BL, TE-6070DV-BL

1. After performing calibration procedure, remove calibrator and top loading adapter. Install TE-3000 Cartridge and remove filter holder frame.

2. Carefully center a new filter, rougher side up, on the supporting screen. Properly align the filter on the screen so that when the frame is in position the gasket will form an airtight seal on the outer edges of the filter.

3. Secure the filter with the frame, brass bolts, and washers with sufficient pressure to avoid air leakage at the edges (make sure that the plastic washers are on top of the frame).

4. Wipe any dirt accumulation from around the filter holder with a clean cloth.

Size Selective Inlet Shim Plate Part number TE-6001-24

An anodized aluminum Shim Plate is supplied on top of the 1st stage plate of the SSI and can be seen by opening the body of the SSI. This collection Shim Plate needs to be heavily greased according to the following frequency and procedure.

Cleaning Frequency

Average TSP at Site	Number of Sampling Days	Interval Assuming Every 6th Day Sample
40 ug/m^3	50	10 months
75 ug/m^3	25	5 months
150 ug/m^3	13	3 months
200 ug/m^3	10	2 months

Cleaning of the Shim Plate is done after removal from the SSI.

- To remove the Shim Plate, unlatch the four SSI hooks located on the sides of the SSI body. Slowly tilt back the top inlet half exposing the 9 acceleration nozzles. Tilt the SSI top half until the SSI body support strut drops and locks into the second, fully open, notch and supports the top half of the inlet. Two Shim Plate Clips located on the right and left sides should be rotated 90° to release the fastening pressure on the shim. The Shim Plate should be handled by the edges and slowly lifted vertically to clear the height of the 16 vent tubes and pulled out forward toward the operator. A clean cloth is used to wipe the soiled grease from the Shim Plate. Acetone or any commercially available solvent can be used to clean the Shim Plate to its original state.

- Clean the interior surfaces of the SSI using a clean cloth.
- Place Shim Plate on a clean flat surface away from the rest of the SSI assembly and spray the Shim Plate with a coating of Dow Corning Silicone #316. This grease is available from Tisch Environmental or from your local Dow Corning Distributor.
- Make sure the Shim Plate is clean, and apply a "generous" amount of the silicone spray after shaking the aerosol can. Spray holding the can 8 to 10 inches away. Spray is necessary in the areas which are below the acceleration nozzles. Allow 3 minutes for the solvent in the spray to evaporate leaving the final greased Shim Plate tacky, but not slippery. After drying, a cloudy film is visible, with a film thickness at least twice the diameter of the particles to be captured. Overspraying with the silicone will not hurt the performance of the SSI, so when in doubt, apply more silicone spray.
- Before reinserting the greased Shim Plate, wipe off all interior surfaces of the SSI and brush any loose dirt or insects off the Bug Screen located below the removable Shim Plate.
- Lift the greased Shim Plate by the edges and place it on the SSI 1st stage plate over top of the vent tubes with the greased side up in reverse order of the above removal procedure. Swing the two Shim Plate Clips over the edge of the greased Shim Plate to hold it securely in place.
- Close the SSI making sure of a good snug fit. Latch the 4 hooks firmly in place.

5. Close PM10 Inlet carefully and secure with all hooks and catches.

6. Make sure all cords are plugged into their appropriate receptacles and on all VFC systems make sure the clear tubing between the filter holder pressure tap and the bulkhead fitting is connected (be careful not to pinch tubing when closing door).

7. Prepare the Timer: See Timer Instructions on page 10, 11, and 12.

8. At the end of the sampling period, remove the frame to expose the filter. Carefully remove the exposed filter from the supporting screen by holding it gently at the ends (not at the corners). Fold the filter lengthwise so that sample touches sample.

9. It is always a good idea to contact the lab you are dealing with to see how they may suggest you collect the filter and any other information that they may require.

VERIFICATION OF PROPER OPERATION

TE-6070, TE-6070D, TE-6070-BL, TE-6070D-BL

Mass Flow Controlled High Volume PM10 Systems

1. Be certain the correlation coefficient is greater than .990

2. There must be three Qa numbers in the range for PM10 (1.02 to 1.24 m^3/min), it is suggested to have one high number, three in the range, and one low number.

3. After collecting filter and Recorder chart make sure that the chart is close to the SSP of the sampler. The sampler must be between 36 to 44 CFM or 1.02 to 1.24 m^3/min.

4. After calculating the total volume, the final result must be in the range of 1.02 to 1.24 m^3/min with this formula: **1/m((I)[Sqrt(Tav/Pav)]- b)**.

VERIFICATION OF PROPER OPERATION

TE-6070V, TE-6070DV, TE-6070V-BL, TE-6070DV-BL

Volumetric Flow Controlled High Volume PM10 Systems

1. After calibration, the % difference for each calibration point must be less than or equal to 3 or 4% per EPA guidelines.

2. There must be three Qa numbers in the range for PM10 (1.02 to 1.24 m^3/min), it is suggested to have one high number, three in the range, and one low number.

3. The Look Up Table reading must be between 36 to 44 CFM or 1.02 to 1.24 m^3/min.

4. For the VFC systems to operate efficiently the motor should run at full voltage; 110 to 120 volts.

Troubleshooting/Corrective Maintenance Procedures

The following is a list of possible problems and the corrective measures.

Shelter: There is nothing on the anodized aluminum shelter that can wear out. In the event a system is dropped or blown over, some shelter parts may become bent. Simply re-shape the bent components or replace them as necessary.
Blower Motor: If the blower motor does not function, perform the following test: 1. Unplug the motor from the flow control device or timer. 2. Plug the motor directly into line voltage. If motor does not operate when plugged directly into line voltage, replace with new motor. If motor operates when plugged directly into line voltage then: See "Electrical Hook-Up" schematic. If motor still does not work, see timer and flow controller instructions.
Dickson Continuous/Flow Pressure Recorder: Not inking properly: replace pen. If pen arm is bent or pen arm lifter is damaged, thereby not allowing pen point to contact chart, replace the pen arm or pen arm lifter as necessary. A tight door seal is necessary to prevent drying of pen, replace if necessary. If pen does not respond properly to pressure/flow signal one of two solutions are available: 1. No rotation of chart indicates a defective chart drive. Replace as necessary. 2. Out of adjustment flow indications may exist if one adjusts the "adjustment screw" beyond its range. This condition allows the bellows to make contact with the chart drive thereby making the bellow movement inaccurate. Factory re-adjustment is necessary.
Filter holder: Two gaskets make contact with the filter holder. The 8" x 10" gasket seals between the shelter base pan and the flange of the filter holder. If this seal is compromised, replace the 8"x 10" gasket. The lower section of the filter holder is sealed against the blower with a round neoprene rubber gasket. This gasket should be replaced if any leakage is evident.
Filter Media Holder: The filter media holder uses the 8" x 10" gasket to seal between it and the filter holder. Another 8" x 10" gasket is also used on the filter media holder to seal between the filter hold-down frame and the filter media itself. If leakage is evident, inspect the gasket for foreign objects and replace as necessary.
Timer: If the timer does not activate the system at the desired time, see "Electrical Hookup Schematic" and timer instructions.
Size Selective Inlet: Inlet does not fit onto shelter: it is critical to install in inlet in a vertical path onto the shelter. Many times it will take two people to gently lower the inlet onto the shelter. If the holes in the sides of the shelter do not exactly line up with holes in Inlet shelter pan, it may be necessary to gently file away a small amount of material to align the holes. Most often the inlet holes will align by simply moving the inlet relative to the shelter until alignment. If the inlet hood does not fit onto acceleration plate, be sure that the spacers are not tightened until all of the washers, screws and spacers are loosely assembled. If inlet does not open properly, be sure the strut is in correct position and strut slot is aligned with shoulder bolt. If the top tub and bottom tub do not seal together, be sure alignment pin in top tub goes into alignment pin "hole" in bottom tub. It is also necessary that the alignment pins on 1st stage plate are aligned with the alignment pin "holes" on bottom tub. Adjustment hooks are provided to assure a seal between the top and bottom tube. To adjust, loosen nut with 3/8" wrench, adjust hook length until a tight seals develops then tighten nut. Shim plate clips are provided to assure the shim plate rests tightly against the first stage plate. Six adjustment screws and catches are provided to insure the seal between the inlet top section and the shelter base pan. Adjust catches by

loosening the nuts with 3/8 wrench, adjust catch length until it seals then tighten. Do this for all 6 catches. A shelter base pan gasket 16"x 16" is provided to seal between the shelter base pan and inlet base pan. If a leak develops, replace this gasket. All gaskets should be inspected for age or misuse. Replace as necessary.

ROUTINE MAINTENANCE

TE-6000 Series, TE-6070, TE-6070D, TE-6070BL, TE-6070D-BL, TE-6070V, TE-6070DV, TE-6070V-BL, TE-6070DV-BL PM10 Samplers:

A regular maintenance schedule will allow a monitoring network to operate for longer periods of time without system failure. Many users find the adjustments in routine maintenance frequencies are necessary due to the operational demands on their sampler(s). We recommend that the following cleaning and maintenance activities be observed until a stable operating history of the sampler has been established.

1. Inspect all gaskets (including motor cushion) to assure they are in good shape and that they seal properly. For the PM-10 Inlet to seal properly, all gaskets must function properly and retain their resilience. Replace when necessary.

2. Power cords should be periodically inspected for good connections and for cracks (replace if necessary).

   CAUTION: Do not allow power cord or outlets to be immersed in water.

3. Inspect the filter screen and remove any foreign deposits.

4. Inspect the filter media holder frame gasket each sample period. This gasket must make an airtight seal.

5. For Brush type systems: Check or replace motor brushes every 300 to 500 hours. If motor has exhausted brush changes, then replace motor.

6. Insure the elapsed time indicator is operating by watching under power.

7. Be certain the continuous flow recorder pen is making contact with the chart and depositing ink each sample period. Be sure the door is sealed completely. Tubing should be inspected for crimps or cracks. Replace when necessary.

8. Clean shim plate periodically, excess dirt will cause false reading and bounce of heavier particulate. See Section SAMPLER OPERATION

9. Be certain the alignment pins are aligning properly. The upper and lower tubs must have an airtight seal.

Be careful not to bend any parts of inlet out of their original aerodynamic shape, mainly the hood, acceleration nozzle plate, nozzles and vent tubes.

MOTOR BRUSH REPLACEMENT TE-6070, TE-6070D MFC PM10

(110v Brush part #TE-33384)
(220v Brush part #TE-33378)

CAUTION: Unplug the system from any line voltage sources before any servicing of blower motor assembly.

1. Remove the blower motor flange by removing the four bolts. This will expose gasket and the TE-116311 motor (220v Motor TE-116312).
2. Rotate the assembly on it's side, loosen the cord retainer and then push cord into housing and at the same time let motor slide out exposing the brushes.
3. Looking down at motor, there are 2 brushes, one on each side. Carefully pry the brass tabs (the tabs are pushed into end of brush) away from the expended brushes and toward the armature. Pry the tabs until they dislodge from the brushes.
4. With a screwdriver loosen and remove brush holder clamps and release TE-33384 brushes. Carefully, pull the tabs from expended brushes.
5. Slide the tabs into tab slot of new TE-33384 brush.
6. Push brush carbon against armature until brush housing falls into brush slot on motor.
7. Put brush holder clamps back onto brushes.
8. Make sure the tabs are firmly seated into tab slot. Check field wires for good connections.
9. Insert the motor by placing housing over while pulling power cord out of housing. Be certain not to pinch the motor wires with the motor spacer ring.
10. Secure power cord with the cord retainer cap.
11. Replace blower motor flange on top of motor making sure to center gasket.

****IMPORTANT**** To enhance motor life:

1. Change brushes before brush shunt touches armature.
2. Seat new brushes by applying 50% voltage for 10 to 15 minutes, the TE-5075 brush break in device allows for the 50% voltage.

MOTOR BRUSH REPLACEMENT TE-6070V, TE-6070DV VFC PM10

(110v Brush part #TE-33392)
(220v Brush part #TE-33378)

CAUTION: Unplug the unit from any line voltage sources before any servicing of blower motor assembly.

1. Remove the VFC device by removing the eight bolts. This will expose the gasket and the TE-115923 motor (220v Motor TE-116111).
2. Rotate the assembly on side, loosen the cord retainer and then push cord into housing and at the same time let motor slide out exposing the brushes.
3. Looking down at motor, there are 2 brushes, one on each side. Carefully pry the brass tabs (the tabs are pushed into end of brush) away from the expended brushes and toward the armature. Pry the tabs until they dislodge from the brushes.
4. With a screwdriver loosen and remove brush holder clamps and release TE-33392 brushes. Carefully, pull the tabs from expended brushes.
5. Carefully slide the tabs into tab slot of new TE-33392 brush.
6. Push brush carbon against armature until brush housing falls into brush slot on motor.
7. Put brush holder clamps back onto brushes.
8. Make sure the tabs are firmly seated into tab slot. Check field wires for good connections.
9. Insert the motor by placing housing over while pulling power cord out of housing. Be certain not to pinch the motor wires with the motor spacer ring.
10. Secure power cord with the cord retainer cap.
11. Replace VFC device on top of motor making sure to align gasket.

****IMPORTANT**** To enhance motor life:

2. Change brushes before brush shunt touches armature.
2. Seat new brushes by applying 50% voltage for 10 to 15 minutes, the TE-5075 brush break in device allows for the 50% voltage.

DESCRIPTION OF METHOD - APPENDIX J PART 50

Code of Federal Regulations July 1, 1998

Appendix J--Reference Method for the Determination of Particulate Matter as PM10 in the Atmosphere

1.0 Applicability.

1.1 This method provides for the measurement of the mass concentration of particulate matter with an aerodynamic diameter less than or equal to a nominal 10 micrometers (PM10) in ambient air over a 24-hour period for purposes of determining attainment and maintenance of the primary and secondary national ambient air quality standards for particulate matter specified in Sec. 50.6 of this chapter. The measurement process is nondestructive, and the PM10 sample can be subjected to subsequent physical or chemical analyses. Quality assurance procedures and guidance are provided in Part 58, Appendices A and B, of this chapter and in References 1 and 2.

2.0 Principle.

2.1 An air sampler draws ambient air at a constant flow rate into a specially shaped inlet where the suspended particulate matter is inertially separated into one or more size fractions within the PM10 size range. Each size fraction in the PM10 size range is then collected on a separate filter over the specified sampling period. The particle size discrimination characteristics (sampling effectiveness and 50 percent cutpoint) of the sampler inlet are prescribed as performance specifications in Part 53 of this chapter.

2.2 Each filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain due to collected PM10. The total volume of air sampled, corrected to EPA reference conditions (25 deg. C, 101.3 kPa), is determined from the measured flow rate and the sampling time. The mass concentration of PM10 in the ambient air is computed as the total mass of collected particles in the PM10 size range divided by the volume of air sampled, and is expressed in micrograms per standard cubic meter (micro-g/ std m^3). For PM10 samples collected at temperatures and pressures significantly different from EPA reference conditions, these corrected concentrations sometimes differ substantially from actual concentrations (in micrograms per actual cubic meter), particularly at high elevations. Although not required, the actual PM10 concentration can be calculated from the corrected concentration, using the average ambient temperature and barometric pressure during the sampling period.

2.3 A method based on this principle will be considered a reference method only if (a) the associated sampler meets the requirements specified in this appendix and the requirements in Part 53 of this chapter, and (b) the method has been designated as a reference method in accordance with Part 53 of this chapter.

3.0 Range.

3.1 The lower limit of the mass concentration range is determined by the repeatability of filter tare weights, assuming the nominal air sample volume for the sampler. For samplers having an automatic filter-changing mechanism, there may be no upper limit. For samplers that do not have an automatic filter-changing mechanism, the upper limit is determined by the filter mass loading beyond which the sampler no longer maintains

the operating flow rate within specified limits due to increased pressure drop across the loaded filter. This upper limit cannot be specified precisely because it is a complex function of the ambient particle size distribution and type, humidity, filter type, and perhaps other factors. Nevertheless, all samplers should be capable of measuring 24-hour PM10 mass concentrations of at least 300 micro-g/std m^3 while maintaining the operating flow rate within the specified limits.

4.0 Precision.

4.1 The precision of PM10 samplers must be 5 micro-g/m^3 for PM10 concentrations below 80 micro-g/m^3 and 7 percent for PM10 concentrations above 80 micro-g/m^3, as required by Part 53 of this chapter, which prescribes a test procedure that determines the variation in the PM10 concentration measurements of identical samplers under typical sampling conditions. Continual assessment of precision via collocated samplers is required by Part 58 of this chapter for PM10 samplers used in certain monitoring networks.

5.0 Accuracy.

5.1 Because the size of the particles making up ambient particulate matter varies over a wide range and the concentration of particles varies with particle size, it is difficult to define the absolute accuracy of PM10 samplers. Part 53 of this chapter provides a specification for the sampling effectiveness of PM10 samplers. This specification requires that the expected mass concentration calculated for a candidate PM10 sampler, when sampling a specified particle size distribution, be within +/-10 percent of that calculated for an ideal sampler whose sampling effectiveness is explicitly specified. Also, the particle size for 50 percent sampling effectiveness is required to be 10+/-0.5 micrometers. Other specifications related to accuracy apply to flow measurement and calibration, filter media, analytical (weighing) procedures, and artifact. The flow rate accuracy of PM10 samplers used in certain monitoring networks is required by Part 58 of this chapter to be assessed periodically via flow rate audits.

6.0 Potential Sources of Error.

6.1 Volatile Particles. Volatile particles collected on filters are often lost during shipment and/or storage of the filters prior to the post-sampling weighing[3]. Although shipment or storage of loaded filters is sometimes unavoidable, filters should be reweighed as soon as practical to minimize these losses.

6.2 Artifacts. Positive errors in PM10 concentration measurements may result from retention of gaseous species on filters[4,5]. Such errors include the retention of sulfur dioxide and nitric acid. Retention of sulfur dioxide on filters, followed by oxidation to sulfate, is referred to as artifact sulfate formation, a phenomenon which increases with increasing filter alkalinity[6]. Little or no artifact sulfate formation should occur using filters that meet the alkalinity specification in section 7.2.4. Artifact nitrate formation, resulting primarily from retention of nitric acid, occurs to varying degrees on many filter types, including glass fiber, cellulose ester, and many quartz fiber filters[5,7,8,9,10]. Loss of true atmospheric particulate nitrate during or following sampling may also occur due to dissociation or chemical reaction. This phenomenon has been observed on Teflon(R) filters[8] and inferred for quartz fiber filters[11,12]. The magnitude of nitrate artifact errors in PM10 mass concentration measurements will vary with location and

ambient temperature; however, for most sampling locations, these errors are expected to be small.

6.3 Humidity. The effects of ambient humidity on the sample are unavoidable. The filter equilibration procedure in section 9.0 is designed to minimize the effects of moisture on the filter medium.

6.4 Filter Handling. Careful handling of filters between presampling and postsampling weighings is necessary to avoid errors due to damaged filters or loss of collected particles from the filters. Use of a filter cartridge or cassette may reduce the magnitude of these errors. Filters must also meet the integrity specification in section 7.2.3.

6.5 Flow Rate Variation. Variations in the sampler's operating flow rate may alter the particle size discrimination characteristics of the sampler inlet. The magnitude of this error will depend on the sensitivity of the inlet to variations in flow rate and on the particle distribution in the atmosphere during the sampling period. The use of a flow control device (section 7.1.3) is required to minimize this error.

6.6 Air Volume Determination. Errors in the air volume determination may result from errors in the flow rate and/or sampling time measurements. The flow control device serves to minimize errors in the flow rate determination, and an elapsed time meter (section 7.1.5) is required to minimize the error in the sampling time measurement.

7.0 Apparatus.

7.1 PM10 Sampler.

7.1.1 The sampler shall be designed to:

a. Draw the air sample into the sampler inlet and through the particle collection filter at a uniform face velocity.
b. Hold and seal the filter in a horizontal position so that sample air is drawn downward through the filter.
c. Allow the filter to be installed and removed conveniently.
d. Protect the filter and sampler from precipitation and prevent insects and other debris from being sampled.
e. Minimize air leaks that would cause error in the measurement of the air volume passing through the filter.
f. Discharge exhaust air at a sufficient distance from the sampler inlet to minimize the sampling of exhaust air.
g. Minimize the collection of dust from the supporting surface.

7.1.2 The sampler shall have a sample air inlet system that, when operated within a specified flow rate range, provides particle size discrimination characteristics meeting all of the applicable performance specifications prescribed in Part 53 of this this chapter. The sampler inlet shall show no significant wind direction dependence. The latter requirement can generally be satisfied by an inlet shape that is circularly symmetrical about a vertical axis.

7.1.3 The sampler shall have a flow control device capable of maintaining the sampler's operating flow rate within the flow rate limits specified for the sampler inlet over normal variations in line voltage and filter pressure drop.

7.1.4 The sampler shall provide a means to measure the total flow rate during the sampling period. A continuous flow recorder is recommended but not required. The flow measurement device shall be accurate to +/-2 percent.

7.1.5 A timing/control device capable of starting and stopping the sampler shall be used to obtain a sample collection period of 24 +/-1 hr (1,440 +/-60 min). An elapsed time meter, accurate to within +/-15 minutes, shall be used to measure sampling time. This meter is optional for samplers with continuous flow recorders if the sampling time measurement obtained by means of the recorder meets the +/-15 minute accuracy specification.

7.1.6 The sampler shall have an associated operation or instruction manual as required by Part 53 of this chapter which includes detailed instructions on the calibration, operation, and maintenance of the sampler.

7.2 Filters.

7.2.1 Filter Medium. No commercially available filter medium is ideal in all respects for all samplers. The user's goals in sampling determine the relative importance of various filter characteristics (e.g., cost, ease of handling, physical and chemical characteristics, etc.) and, consequently, determine the choice among acceptable filters. Furthermore, certain types of filters may not be suitable for use with some samplers, particularly under heavy loading conditions (high mass concentrations), because of high or rapid increase in the filter flow resistance that would exceed the capability of the sampler's flow control device. However, samplers equipped with automatic filter-changing mechanisms may allow use of these types of filters. The specifications given below are minimum requirements to ensure acceptability of the filter medium for measurement of PM10 mass concentrations. Other filter evaluation criteria should be considered to meet individual sampling and analysis objectives.

7.2.2 Collection Efficiency. >/=99 percent, as measured by the DOP test (ASTM-2986) with 0.3 micro-m particles at the sampler's operating face velocity.

7.2.3 Integrity. +/-5 micro-g/m^3 (assuming sampler's nominal 24-hour air sample volume). Integrity is measured as the PM10 concentration equivalent corresponding to the average difference between the initial and the final weights of a random sample of test filters that are weighed and handled under actual or simulated sampling conditions, but have no air sample passed through them (i.e., filter blanks). As a minimum, the test procedure must include initial equilibration and weighing, installation on an inoperative sampler, removal from the sampler, and final equilibration and weighing.

7.2.4 Alkalinity. 0.5 m^3/min). Lower volume samplers (flow rates).

7.3 Flow Rate Transfer Standard. The flow rate transfer standard must be suitable for the sampler's operating flow rate and must be calibrated against a primary flow or volume standard that is traceable to the National Bureau of Standards (NBS). The flow rate transfer standard must be capable of measuring the sampler's operating flow rate with an accuracy of +/- 2 percent.

7.4 Filter Conditioning Environment.

7.4.1 Temperature range: 15 to 30 C.

7.4.2 Temperature control: +/- 3C.

7.4.3 Humidity range: 20% to 45% RH.

7.4.4 Humidity control: +/-5% RH.

7.5 Analytical Balance. The analytical balance must be suitable for weighing the type and size of filters required by the sampler. The range and sensitivity required will depend on the filter tare weights and mass loadings. Typically, an analytical balance with a sensitivity of 0.1 mg is required for high volume samplers (flow rates > 0.5 m^3/min). Lower volume samplers (flow rates < 0.5 m^3/min) will require a more sensitive balance.

8.0 Calibration

8.1 General Requirements.

8.1.1 Calibration of the sampler's flow measurement device is required to establish traceability of subsequent flow measurements to a primary standard. A flow rate transfer standard calibrated against a primary flow or volume standard shall be used to calibrate or verify the accuracy of the sampler's flow measurement device.

8.1.2 Particle size discrimination by inertial separation requires that specific air velocities be maintained in the sampler's air inlet system. Therefore, the flow rate through the sampler's inlet must be maintained throughout the sampling period within the design flow rate range specified by the manufacturer. Design flow rates are specified as actual volumetric flow rates, measured at existing conditions of temperature and pressure (Qa). In contrast, mass concentrations of PM10 are computed using flow rates corrected to EPA reference conditions of temperature and pressure (Qstd).

8.2 Flow Rate Calibration Procedure.

8.2.1 PM10 samplers employ various types of flow control and flow measurement devices. The specific procedure used for flow rate calibration or verification will vary depending on the type of flow controller and flow indicator employed. Calibration in terms of actual volumetric flow rates (Qa) is generally recommended, but other measures of flow rate (eg. Qstd) may be used provided the requirements of section 8.1 are met. The general procedure given here is based on actual volumetric flow units (Qa) and serves to illustrate the steps involved in the calibration of a PM10 sampler. Consult the sampler manufacturer's instruction manual and Reference 2 for specific guidance on calibration. Reference 14 provides additional information on the use of the commonly used measures of flow rate and their interrelationships.

8.2.2 Calibrate the flow rate transfer standard against a primary flow or volume standard traceable to NBS. Establish a calibration relationship (eg. An equation or family of curves) such that traceability to the primary standard is accurate to within 2 percent over the expected range of ambient conditions (ie temperatures and pressures) under which the transfer standard will be used. Recalibrate the transfer standard periodically.

8.2.3 Following the sampler manufacturer's instruction manual remove the sampler inlet and connect the flow rate transfer standard to the sampler such that the transfer standard accurately measures the sampler's flow rate. Make sure there are no leaks between the transfer standard and the sampler.

8.2.4 Choose a minimum of three flow rates (actual m^3/min), spaced over the acceptable flow rate range specified for the inlet (see 7.1.2) that can be obtained by suitable adjustment of the sampler flow rate. In accordance with the sampler manufacturer's instruction manual, obtain or verify the calibration relationship between the flow rate (actual m^3/min) as indicated by the transfer standard and the sampler's flow indicator response. Record the ambient temperatures and barometric pressure. Temperature and pressure corrections to subsequent flow indicator readings may be required for certain types of flow measurement

devices. When such corrections are necessary, correctin on an individual or daily basis is preferable. However, seasonal average temperature and average barometric pressure for the sampling site may be incorporated into the sampler calibration to avoid daily corrections. Consult the sampler manufacture's instruction manual and Reference 2 for additional guidance.

8.2.5 Following calibration, verify that the sampler is operation at its design flow rate (actual m^3/min) with a clean filter in place.

8.2.6 Replace the sampler inlet.

9.0 Procedure.

9.1 The sampler shall be operated in accordance with the specific guidance provided in the sampler manufacturer's instruction manual and in Reference 2. The general procedure given here assumes that the sampler's flow rate calibration is based on flow rates at ambient conditions (Qa) and serves to illustrate the steps involved in the operation of a PM10 sampler.

9.2 Inspect each filter for pinholes, particles, and other imperfections, establish a filter information record and assign an identification number to each filter.

9.3 Equilibrate each filter in the conditions environment (see 7.4) for at least 24 hours.

9.4 Following equilibration, weigh each filter and record the presampling weight with the filter identification number.

9.5 Install a preweighed filter in the sampler following the instructions provided in the sampler manufacturer's instruction manual.

9.6 Turn on the sampler and allow it to establish run-temperature conditions. Record the flow indicator reading and, if needed, the ambient temperature and barometric pressure. Determine the sampler flow rate (actual m^3/min) in accordance with the instructions provided in the sampler manufacturer's instruction manual. NOTE- No onsite temperature or pressure measurements are necessary if the sampler's flow indicator does not require temperature or pressure corrections or if seasonal average temperature and average barometric pressure for the sampling site are incorporated into the sampler calibration (see step 8.2.4). If individual or daily temperature and pressure corrections are required, ambient temperature and barometric pressure can be obtained by on-site measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampling site and the airport.

9.7 If the flow rate is outside the acceptable range specified by the manufacturer, check for leaks, and if necessary, adjust the flow rate to the specified setpoint. Stop the sampler.

9.8 Set the timer to start and stop the sampler at appropriate times. Set the elapsed time meter to zero or record the initial meter reading.

9.9 Record the sample information (site location or identification number, sample date, filter identification number, and sampler model and serial number).

9.10 Sample for 24+/- 1 hours.

9.11 Determine and record the average flow rate (Qa) in actual m^3/min for the sampling period in accordance with the instructions provided in the sampler manufacturer's instruction manual. Record the elapsed time meter final reading and, if needed, the average ambient temperature and barometric pressure for the sampling period (see note following set 9.6)

9.12 Carefully remove the filter from the sampler, following the sampler manufacturer's instruction manual. Touch only the outer edges of the filter.

9.13 Place the filter in a protective holder or container (eg. petri dish, glassine envelope, or manila folder).

9.14 Record any factors such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement on the filter information record.

9.15 Transport the exposed sample filter to the filter conditioning environment as soon as possible for equilibration and subsequent weighing.

9.16 Equilibrate the exposed filter in the conditioning environment for at least 24 hours under the same temperature and humidity conditions used for presampling filter equilibration (see 9.3).

9.17 Immediately after equilibration, reweigh the filter and record the postsampling weight with the filter identification number.

8.0 Sampler Maintenance.

10.1 The PM10 Sampler shall be maintained in strict accordance with the maintenance procedures specified in the sampler manufacturer's instruction manual.

9.0 Calculations.

11.1 Calculate the average flow rate over the sampling period corrected to EPA reference conditions as Qstd. When the sampler's flow indicator is calibrated in actual volumetric units (Qa), Qstd is calculated as:

$Qstd = Qa * (Pav/Tav)(Tstd/Pstd)$

Where:

Qstd = average flow rate at EPA reference conditions, std m^3/min;

Qa = average flow rate at ambient conditions, m^3/min;

Pav = average barometric pressure during the sampling period or average barometric pressure for the sampling site, kPa (or mm Hg);

Tav = average ambient temperature during the sampling period or seasonal average ambient temperature for the sampling site, K;

Tstd = standard temperature, defined as 298K;

Pstd = standard pressure, defined as 101.3kPa (or 760 mm Hg).

11.2 Calculate the total volume of air sampled as:

$Vstd = Qstd * T$

Where:

Vstd = total air sampled in standard volume units, std m^3;

T = sampling time, min.

11.3 Calculate the PM10 concentration as:

$PM10 = (Wf - Wi) * 10^6/Vstd$

Where:

PM10 = mass concentration of PM10 micro-g/std m^3

Wf, Wi = final and initial weights of filter collecting PM10 particles, g;

10^6 = conversion of g to micro-g.

Note: If more than one size fraction in the PM10 size range is collected by the sampler, the sum of the net weight gain by each collection filter [Summation (Wf-Wi)] is used to calculate the PM10 mass concentration.

G-858

MAGMAPPER

25309-OM REV. D

Operation Manual

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CE 97

December 3, 1996

Sunnyvale, California, USA

EC DECLARATION OF CONFORMITY

We, Geometrics, Inc.
Geometrics Europe
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Sunnyvale, CA 94089 USA ph:
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6131

declare under our sole responsibility that our portable magnetometers, models G-858 and G-858G to which this declaration relates are in conformity with the following standards:

EN61010-1 :1993/A2: 1995

per the provisions of the **Low Voltage Directive** ***73/231EEC*** of 19 February 1973 as Amended by ***93/68/EEC, Article 13*** of 22 July 1993 and,

EN 55022: 1995, EN50082-2 : 1995, ENV 50140: 1994, ENV 50141 :1994, EN 61000-4-2: 1995, EN 61000-4-4: 1995

per the provisions of the **Electromagnetic Compatibility Directive** ***8913361EEC*** of May 1989 as Amended by ***92131/EEC*** of 28 April 1992 and *93/68-EEC, Article 5* of 22 July 1993.

The Technical documentation required by Annex IV(3) of the Low Voltage Directive is maintained by Christopher Leech of Geometrics Europe (address below).

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Warning

This is a Class A product. In a domestic environment this product may cause radio interference in which case the user may be required to take adequate measures.

Table of Contents

Chapter 1: Introduction

Overview

The model G-858 is a professional quality magnetic mapping tool offering exceptional speed and efficiency. The system presents a "Quick Look" to the operator of up to 5 stacked survey profiles, *as well as a graphical map of the survey grid showing surveyed and unsurveyed portions*. Data is stored in non-volatile memory for playback review and downloading into a host PC. The system includes a comprehensive software package to download, edit and interpolate magnetic data into 2D or 3D contour-ready formats. Hard copy annotated color maps can be produced within minutes after data transfer to the base computer.

The G-858 includes three unique features, each intended to assist the collection of magnetic data. First, the system lets you visualize the survey area beforehand, entering in the desired survey location points. Second, it lets you review your locations and your data during the survey. Finally, the unit allows you to edit data, both in the field and in later processing.

Applications

The G-858 MagMapper may be used to locate buried drums or other underground storage containers; to find pipelines, well-heads and other utilities; to search for unexploded ordnance, discarded weapons or magnetic mines; to look for graves or archeological sites; to study geological structures and faults; to find mineral deposits and aid in the siting of mines and quarries, etc. The fast response of the instrument means that the data may be taken at a brisk walking pace which efficiently covers four to ten times as much ground per hour as prior magnetometers. The high sensitivity means that many potential targets (including voids) which would have been missed with other techniques will stand out clearly and unambiguously.

Features

The G-858 has been designed to greatly simplify magnetic surveying. All of its features are intended to speed up the surveying process and reduce the possibility of mistakes. Toward that end, the following features have been incorporated into the G-858:

- Continuous surveying, where the unit automatically records data at a user-selectable rate, up to 10 readings per second.
- Discrete surveying, where the unit takes a reading upon an operator key-press.
- Four modes of operation: search mode, for performing a random search for anomalies or system test; simple survey, for a simplified method of operation; mapped survey, for the full capability of defining and tracking position as readings are taken; and base station, for collecting data to be used for diurnal corrections.
- Real-time analog sweep display of the current magnetometer reading.
- Up to five separate surveys stored independently.
- Map displays, showing the survey area, with readings plotted in the correct locations.
- Data profile displays, allowing previous data to be reviewed.
- Data editing capability, where data may be deleted and retaken.
- Downloading of data in compressed format to a host PC.
- Host software for editing data positions, and writing a file for 3D surface plotting with 3rd party software, such as WinSurf or GeoSoft.
- Audible tones indicating the field change over the local target, warning of non-valid data, indicating that data was taken and stored, and that location keys have been pressed.
- Storage capacity for more than 250,000 readings and positions, each recorded with the time of the event.
- Logging of data from an RS-232 input port (for example, GPS data).
- Logging of user-defined field notes.

Modes of Operation

Here we present an overview of the modes of operation, along with their advantages and when each should be used.

Search Mode

In Search mode, the magnetometer operates normally, displaying an analog oscilloscope-like trace, with an audible sound whose pitch indicates changes in the field reading (the "woowee" indicator). However, data is not stored in memory. This is useful for manually identifying anomaly locations, much as with a metal detector. It is also useful to check for proper sensor operation and ambient magnetic noise.

Simple Survey Mode

In simple survey mode, the unit keeps track of MARK (start line, and waypoints) and END LINE (end of line) key presses, and the direction of each line. This allows a full and complete survey. Later, after downloading the data into the PC, the MagMap program will attach an x and y coordinate to each reading.

Simple survey mode allows the simplest operation of the G-858, at the expense of a slightly more complicated operation of the PC host software. You must manually keep track of where you are taking data, and enter this information into the host software to locate the readings.

Mapped Survey Mode

Mapped survey allows you to better visualize the survey area than simple survey, and move around within the area in a non-continuous fashion. Using the arrow keys, you may position the cursor anywhere within the map and acquire data. Default cursor movements are programmed into the unit, so if you follow a normal path across the survey area, you may simply press the MARK and END LINE keys as if you were doing a simple survey.

This method allows the easiest operation of the PC host software. You must enter more information into the G-858, however. This mode will track your position for you automatically, assuming you are following a simple path, while also allowing you to change your position manually, when, for example, you reach an obstruction and wish to start again on the other side.

Base Station Mode

In base station mode, the unit will not keep track of changes in position. This is most useful when the unit is being used to collect data for diurnal correction. Both data and the time of the readings are stored in internal memory.

In addition, this mode supports a real-time transfer of data out of the RS232 port as it is being acquired. This is useful if you are using another PC to collect and process the data, for instance, when using the G-858 from a mobile platform. Of course, you may also store the data inside the G-858, with or without real-time transfer.

Magnetic Surveying Checklist

Here we give a quick checklist for performing a magnetic survey. Please see Appendix 1 if you are unfamiliar with magnetic surveying. Subsequent chapters will explain in detail the operation of the G-858 during the survey.

1. Setting up the survey grid

- Designate an individual to be responsible for making a sketch of the survey site, with notes and comments on all relevant objects such as power lines, fences, pipes, and surface debris.
- Establish a base line, which will provide the start or end points for all profile lines. Designate the left hand corner of the base line to be (0,0) for the X and Y axes. Note that the survey lines can run in any direction, but if a choice exists, the preferred direction would be North and South.
- Using the smallest search target size, determine the separation of the profile lines. For small targets such as a one pound ferrous mass with worst case shape and orientation, lines spaced 2 meters apart is a good initial choice.
- Place non-magnetic, brightly colored markers at the start and stop of each profile. If the lines are long or require irregular walking speeds, place a marker at regular intervals (perhaps each 20 or 50 meters) along the profile. These will become fiducial or waypoint entries in the data stream.
- If the survey is to be broken into separate but adjacent areas, it will help you to stitch the sections together if there is at least one profile line of overlap. Also insure that the profiles extend beyond the actual survey boundary by at least 2 or 3 times the estimated target depth.
- Locate the survey area corners and reference them to other surface objects. If the site will be relocated in the future, it may be useful to permanently mark the corners with an iron stake (re-bar) driven down to ground level. Note that these corner stakes are the only magnetic objects that are used on the entire survey site. Flags, cones, stakes and other markers must be carefully inspected to be non-magnetic.

2. Turn on and warm up the G-858, using the procedure described in Chapter 2.. Select the Search Mode, and adjust the sensor for the proper operating orientation, i.e. there should be continuous signal and correct instrument operation in all directions of the survey profiles. The program CSAZ will help to determine the best sensor orientation to avoid dead zones.

3. Demagnetize the magnetometer operator. Using the G-858 in the Search Mode, insure that the operator does not contribute an error greater than 1 nT in any direction. (Refer to the Applications Manual, chapter 4 for a fast, simple, "magnetic swing" procedure that will measure the operator's magnetic cleanliness.) Pay particular attention to the operator shoes, eye glasses, and the removal of rings, keys , belt buckle, and all pocket items. Only a small amount of magnetic material is needed to seriously distort the magnetic data. (Shoes are always suspect and are the closest moving parts to the sensor.)

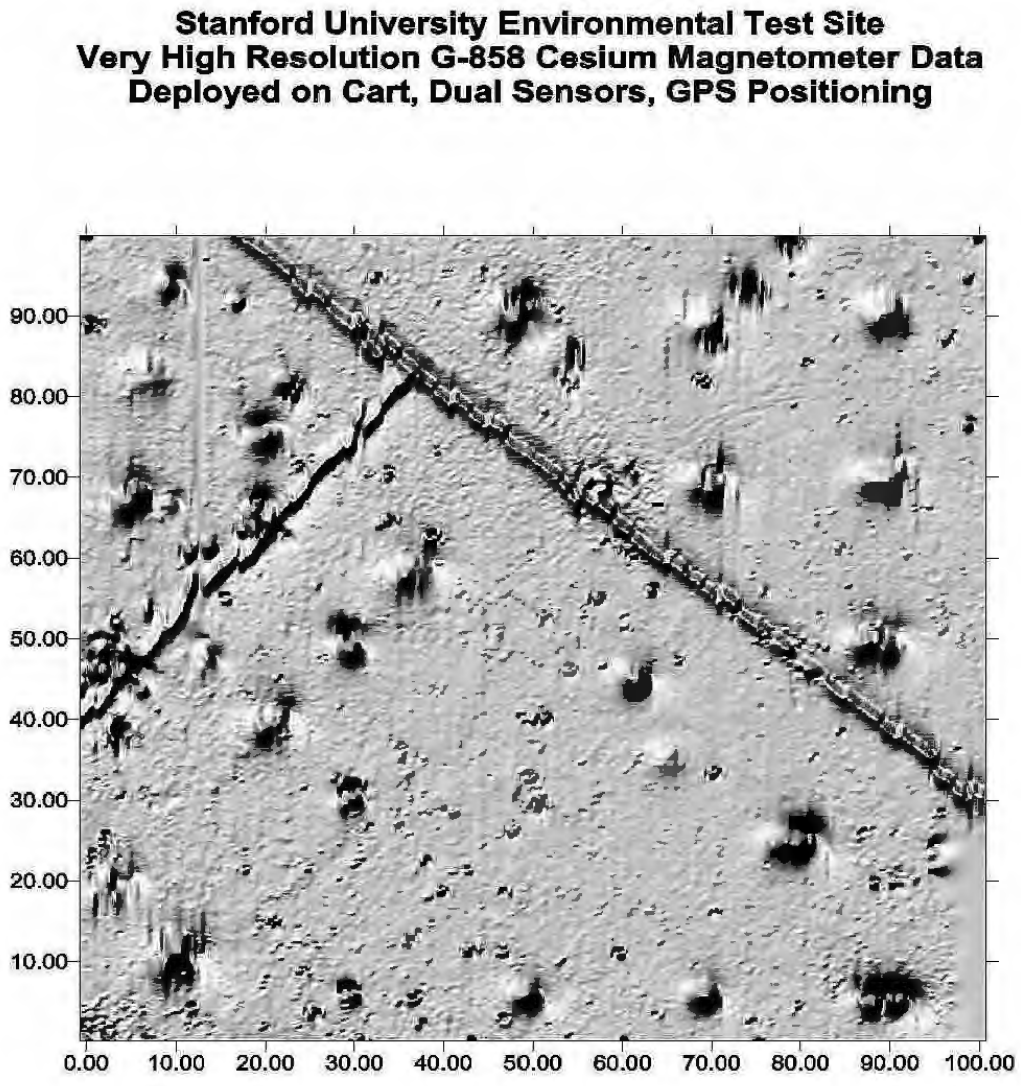
4. Select a survey "Test Profile" line. This profile should be run in each direction at the start and end of each survey day as a check of data repeatability and quality. It is an excellent check of proper system operation and may be useful as "proof of operation" to the end user.

5. Perform the data acquisition for all survey profiles and record the direction of each profile on the survey sketch map. Also record the start and end locations and the direction of the first and last survey profiles for each survey day. This may be duplication of effort, but is independent of the data logged in the instrument and may be very helpful in editing the data during processing.

6. During the course of the survey it is important that the operator has adequate support in finding and staying on the line. However, if the operator is disrupted during data acquisition, the G-858 easily allows data to be deleted and/or retaken. The G-858 has been designed to reduce mistakes and save money.

7. Finally, at the end of the survey, download the data to your host PC via the RS-232 port, edit the positions if necessary, perform diurnal corrections, and convert the file to a suitable output for 3rd party software, such as Surfer for Windows or Geosoft. An example of processed data is shown below.

Surfer for Windows output for an example survey site.



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Chapter 2: Set Up and Operation

This chapter gives an overview of the entire surveying process. It will describe how to set up the instrument, operate in the *Simple Survey* mode, and download the data into the PC for analysis. Please read Chapter 3 as soon as you can to find out more about your G-858 magnetometer.

Unpacking your G-858

The instrument is shipped in a rugged container, with each element carefully packed in foam cells. Please remove all the items in the case. The tables below show the items that should be included.

Part Number	Name	Description
0025306-01	Console	Main magnetometer console, containing electronics, keypad, and display
0025307-01	Battery belt (2 included)	Battery belt for easy carrying of the system batteries. Batteries are installed in the belt
0025332-01	Shoulder harness	Distributes the load of the batteries and console
0025366-01	Battery charger	Charges the batteries
0025386-01	Holster	Holds the end of the staff in vertical mode
0025349-01	Sensor staff assembly	Connect together to form a staff of the desired length and balance the sensor weight
0025367-01	Sensor clamps	Hold the sensor to the staff
0025369-01	Strap clamp assembly	Staff strap connection
0027516-05	Sensor	Measures the magnetic field
0025358-01	Serial cable	Carries data from the G-858 to the PC
0025382-01	Auxiliary belt assembly	Provides more flexibility in positioning sensor staff for greater comfort
28-806-003 0027573-01	Velcro cable locks and cable hanger	Keep the sensor cable neatly attached to the staff
40-304-002	Adapter plug kit	Adapts to various AC power standards
0025376-01	Fuse assembly	Extra fuses for battery belt
0018134-01	Application manual	Describes principles of magnetic surveying
0025309-OM	Operation manual	This document
20-200-300	MagMap PC software	Used to download data to host PC, modify positions, and write output files.
0025370-01	Shipping case	Storage and shipping of the G-858

Items included in G-858.

The following additional items are included with G-858 gradiometers.

0016552-01	Staff “tee” piece	Holds the cross piece at the end of the staff
0016536-03	Cross piece	Forms the perpendicular piece to the staff
0025382-01	Auxiliary belt	Supports the extra weight of the staff
00165539-02	Large counter weight	Replaces the smaller counter balance

Assembly

The photograph below depicts the G-858 in normal usage.

Sensor Staff

The sensor staff consist of 3 identical sections. The sections plug into each other, and are held in place by rubber cams. Plug them together by aligning the cam with the shaft, giving a 1/2 turn twist to lock them together. Install the sensor clamp (with short piece of tubing) with strap clamp on one end of the staff, and the counter balance on the other. Clip the strap to the counterbalance.

G-858 Console

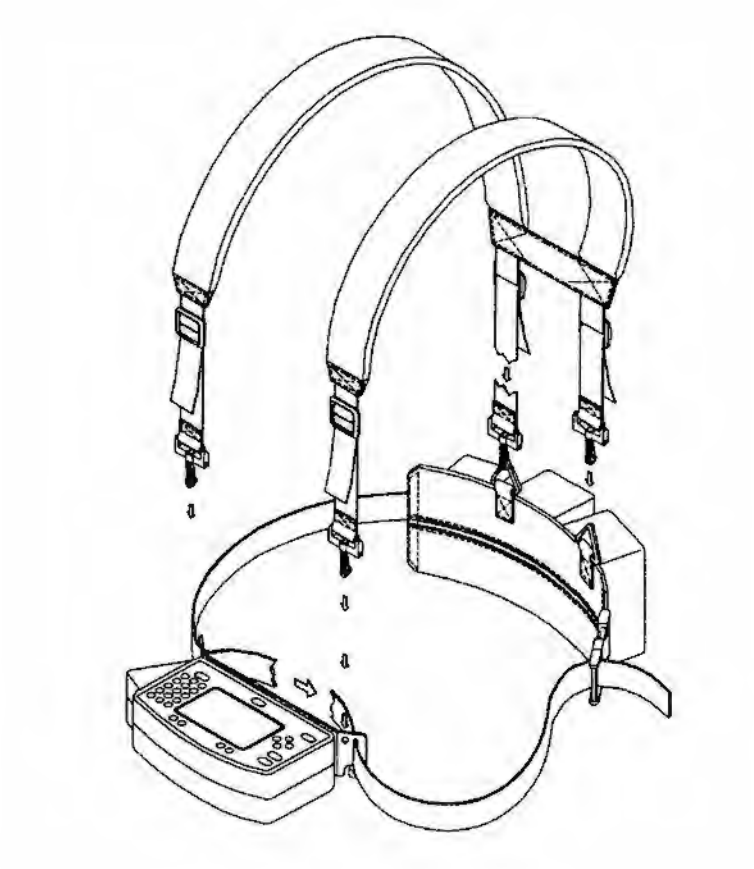
The G-858 console is pictured below. The slots in the spreader bar are designed to slip over the battery belt. The holes are for attaching the front shoulder straps. The connectors are for the power cable, I/O port, and 2 cesium magnetic sensors.

G-858 Console. The upper left connector is the battery connector, the upper right is the serial I/O port, and the two lower connectors are for the sensors. The right-hand sensor connector is used for single magnetometer operation, for the top sensor in the vertical gradient mode of operation, and for the left sensor in the horizontal gradient mode.

Wearing the G-858

The G-858 is designed for comfortably carrying the batteries, console, and sensor while making a magnetic survey.

1. Attach the rear shoulder straps to the battery belt. The hooks on the straps attach to the triangular rings above the batteries. The front and rear straps both adjust, so you can position the straps most comfortably. The Velcro fasteners go over the right shoulder.
2. Put the battery belt around your waist. The belt is adjusted with the sliding lock on the left hand side. Due to the stiffness of the webbing, this may be slightly inconvenient, but will need to be adjusted only once for a particular operator. The belt may be easily taken off by unclipping the bracket.
3. Slide the console onto the front of the battery belt, threading the webbing through the slots. You may find it convenient to thread the extra belt length through the console slots as well. Connect the battery cable between the battery belt and the console.



4. Bring the shoulder straps over your shoulders and connect them to the holes on the console. The adjustments at the front and rear of each strap allow you to position the straps most comfortably. If the straps tend to get pulled off your shoulders, it may be more comfortable to cross them in front. See the photos below.

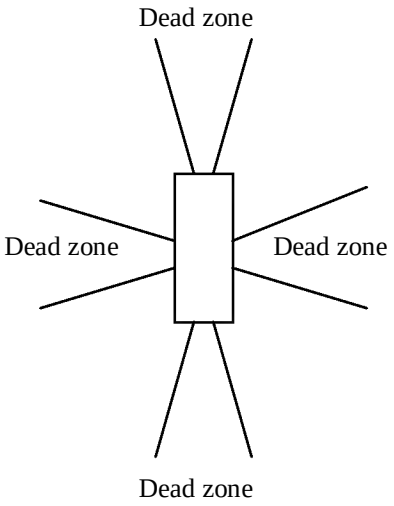
5. The sensor staff strap now should go over your right shoulder. This is recommended even for left handed people as the cables come out of the right side of the console. Thread the staff strap through one or more of the Velcro catches on the shoulder strap. This will keep the strap from tending to slide off of the shoulder.
6. Connect the sensor cable to the console (see the picture on p. 10 to determine which connector(s) on the console to use). Use the velcro cable locks to attach the length of cable to the staff, so it doesn't dangle and get in your way.
7. If you wish to hold the sensor staff vertically, take out the counter balance and use the staff holster provided to support the end of the staff. The large velcro strap on the right shoulder harness may be used to hold the staff in the vertical position.

Note: To remove the system, first unclip the battery belt clasp. Then lift the unit over your head by the tops of the shoulder straps, leaving the console attached to the battery belt.

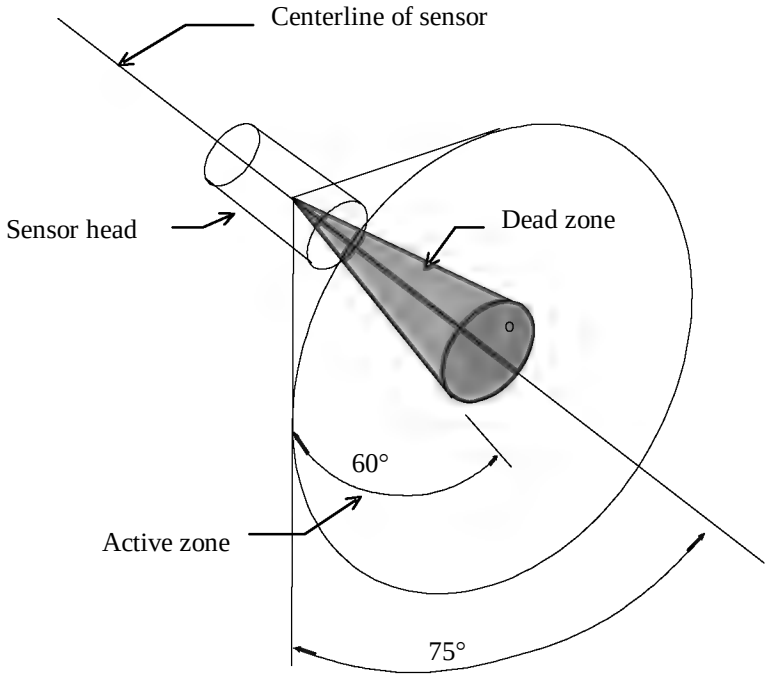
Cesium Sensor Orientation

A cesium sensor is insensitive to magnetic fields in certain directions. This is due to the nature of the operation of the sensor. If the magnetic field direction is within 15 degrees of the optical centerline of the sensor, or within 15 degrees of the plane perpendicular to that (the equatorial plane), the sensor will read 0.00 for the magnetic field value. See the sketch below.

A program is provided to help you determine what orientation is best for the sensor, given the dip angle of the Earth's magnetic field where the survey will be taking place. See Appendix 2 for more details.



Profile View



3D View

Operating the G-858

Charging the Batteries

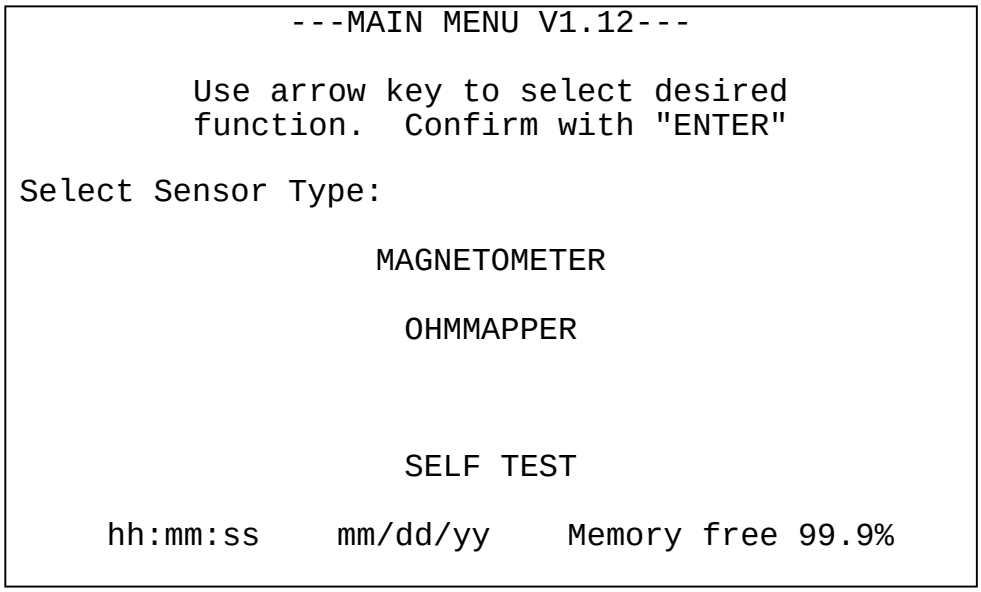
Use the supplied charger to charge the batteries before use. A full charge will take about 6-8 hours. Connect the battery charger directly to the cable coming out of the battery belt. Two battery belts are supplied so you can continue working after one has discharged. The unit will operate 6 hours on one charge, so with two belts, you can work up to 12 hours (at 25° C). As a gradiometer, battery life is reduced to 3.5 hours. At -10° C, battery life is further reduced 33 %.

Note: To best maintain battery life, you should periodically charge the batteries (about every 4 months) if the unit is not in use.

Powering on and off.

After charging the battery, connect the console to the battery belt cable. This cable may be tucked into the pouch in the battery belt when not in use.

Press the POWER key to power the unit up. You may need to adjust the display contrast (keys marked LIGHT and DARK) in order to see the display. The menu first shown is the Main Menu:



Pressing the POWER key when the Main Menu is displayed will shut the unit off. This logging console is used with two of Geometrics' products, the G-858 Magnetometer and the Ohmmapper. If the either MAGNETOMETER or OHMMAPPER menus have been selected from this menu, the POWER key will also shut the unit off in those menus. At other times, the POWER key is ignored

Note: To shut the unit off, press ESC until the MAIN MENU, G-858 MAGNETOMETER or OHMMAPPER menus are shown, then press POWER.

Try not to disconnect the battery cable during use. If the battery cable is disconnected, some of the most recent data may be lost. Every effort has been made to protect your data in this event. However, depending upon what the microprocessor was doing at the time power was interrupted, data corruption may occur.

The unit will power itself off when the batteries reach a low voltage condition. Data back to the last position marker will be lost, however.

Note: The gauges on the left of the display show the battery power and memory left in the G-858. You should keep track of these indicators.

High-pitched sounds coming from the G-858 are normal. Capacitors used on the internal circuit boards exhibit a piezo-electric effect, and create the buzzing noises.

Note: You should allow the sensor to warm up for 5 to 15 minutes before starting the survey, depending upon ambient temperature. During the warm up period, the unit may display an "inoperative sensor" message. If this happens, simply unplug the sensor and plug it back in, or cycle the power of the G-858. See the later section "Warming up the G-858" later in this chapter for the proper procedure.

Using the menus

Selecting fields in a menu

Menu fields are highlighted by pressing the up and down arrow keys. There are 3 types of fields which may be highlighted.

Scroll list.

A scroll list is indicated by the angle brackets, < >, on each side (see the "Baud rate" field in the menu example below). Press the left and right arrow keys to scroll through a list of options. You do not need to press the ENTER key. Simply move out of the field with the up or down arrow key, or press ESC to move up an entire menu level.

Numeric entry field.

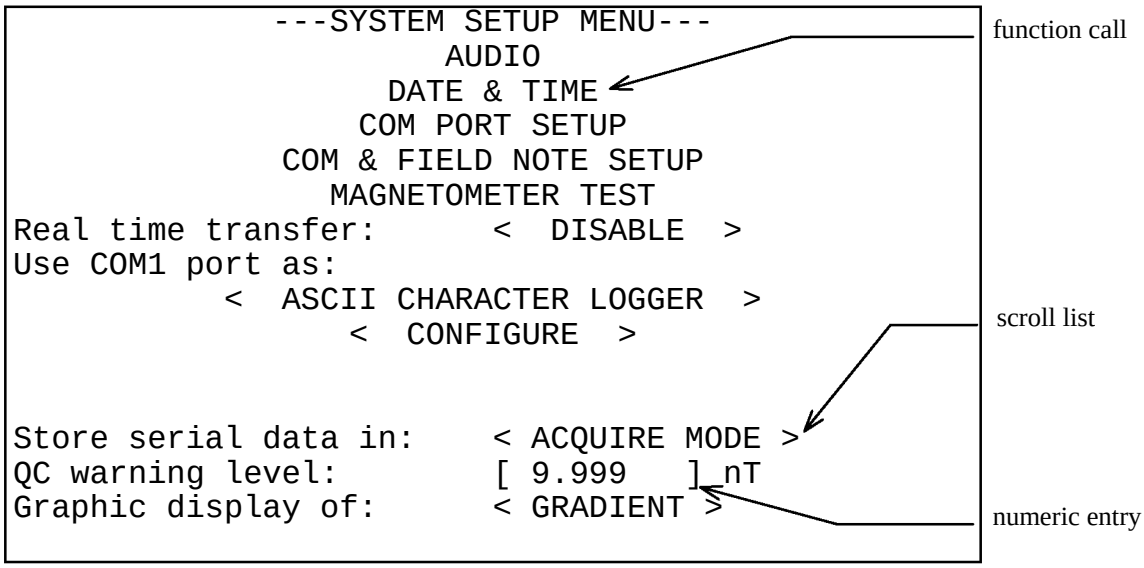
A numberic entry field is indicated by square brackets, [ ], on each side (see the "QC warning level" field in the menu example below). Press the DEL key to delete the number that is there, type a new number, and press ENTER. Using the up and down arrow keys to move out of this field without first pressing ENTER will cause the numeric value to return to the last value.

Note: Don't forget to press the ENTER key after entering the desired value. You can also move the cursor within a field by pressing the arrow keys to select and change individual digits.

Function calls.

Function calls are indicated by a text only box, with no angle or square brackets (see the AUDIO, DATE & TIME, and SELF TEST fields in the menu example below). Pressing ENTER in these fields will cause the indicated action to occur.

Menu Example:

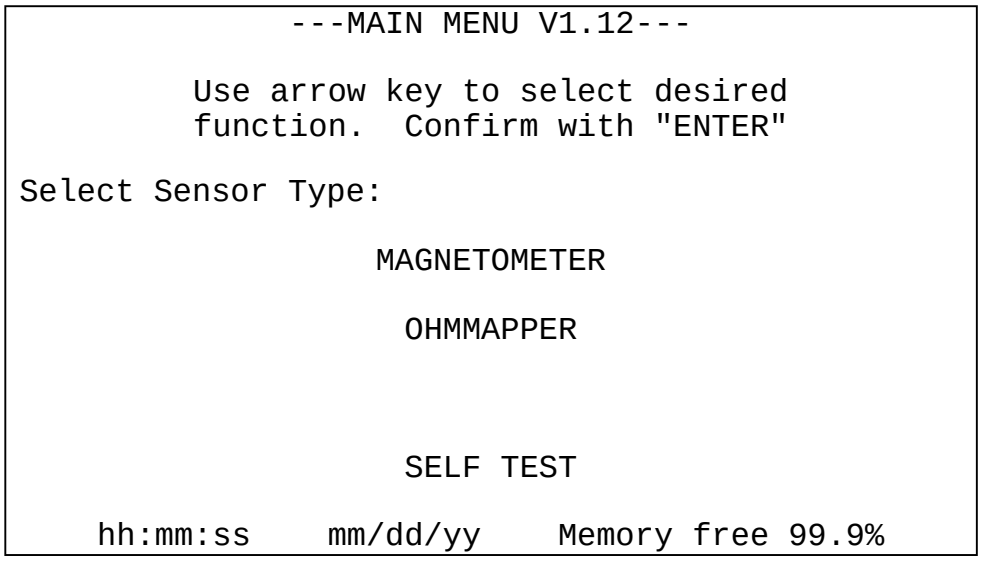


Moving through menus

In this document, “selecting” an item means highlighting it with the arrow keys and pressing ENTER. “Scrolling” to a value refers to highlighting the field item and pressing the left or right arrow keys until the desired value is displayed.

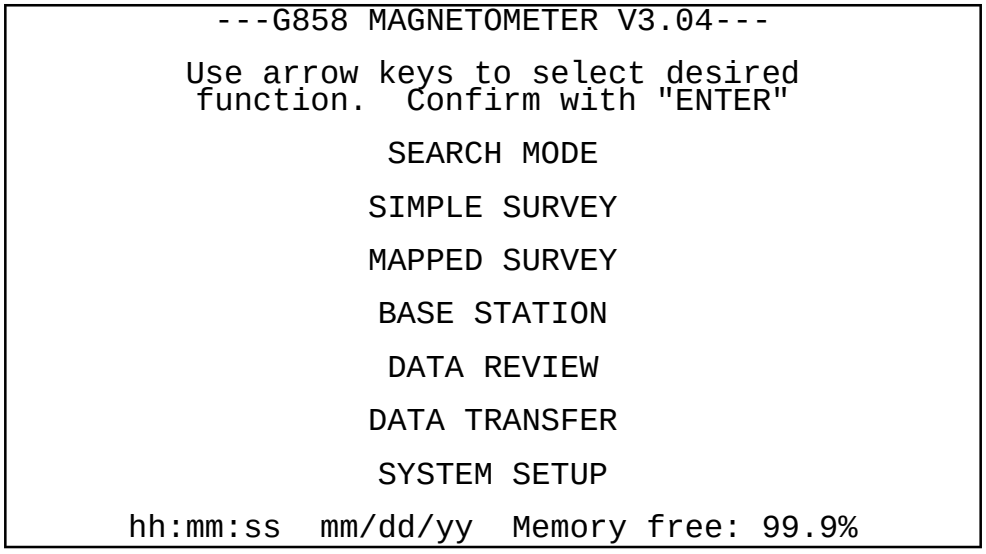
Press the ESC key to back up a menu level.

The first menu displayed on power up is the main menu, shown below.



Main Menu

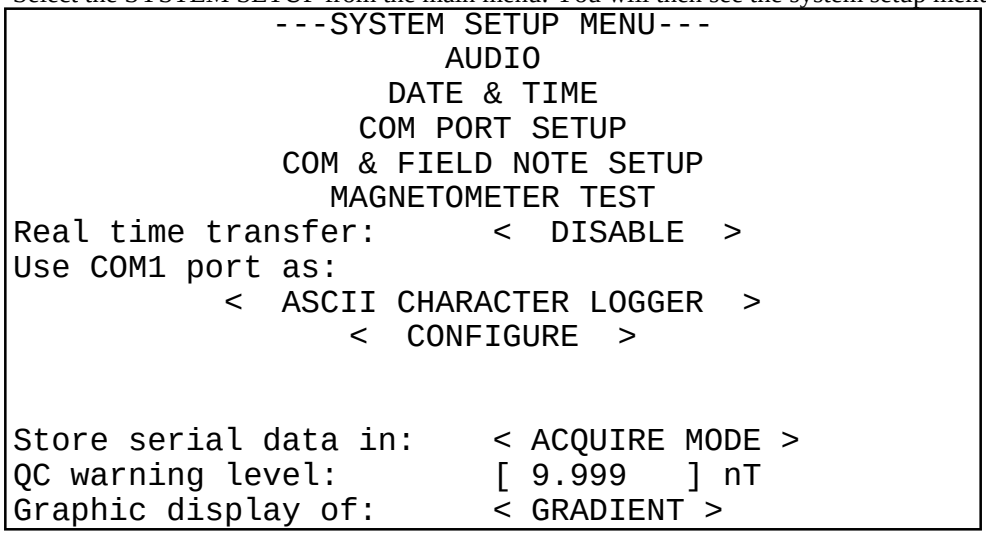
From this Main Menu press the arrow key until MAGNETOMETER is highlited and press ENTER to selet G-858 Magnetometer operation. The following menu will appear.



G-858 Manetometer menu.

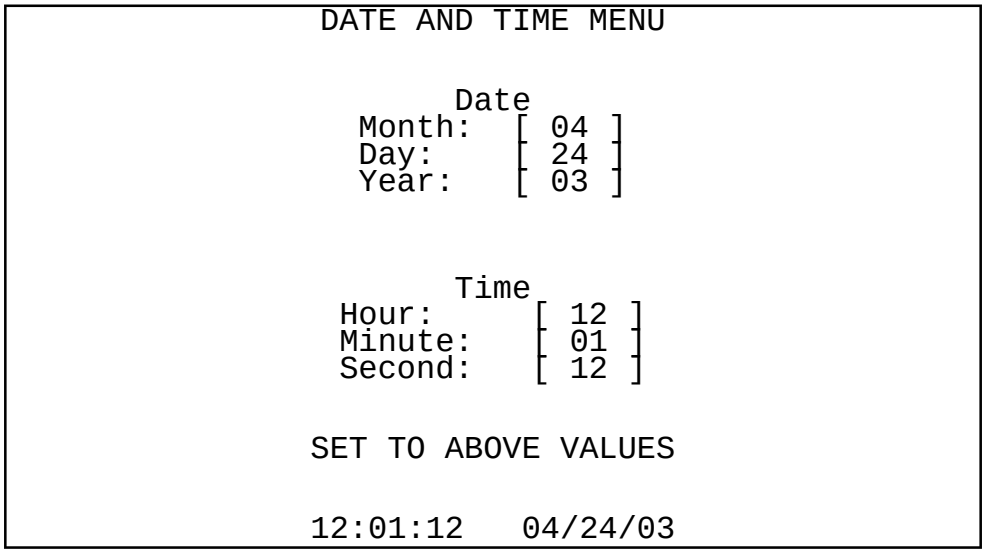
Setting up the G-858

Select the SYSTEM SETUP from the main menu. You will then see the system setup menu.



System Setup Menu. The last line is shown only on gradiometers.

Select DATE AND TIME, showing the date and time menu below.



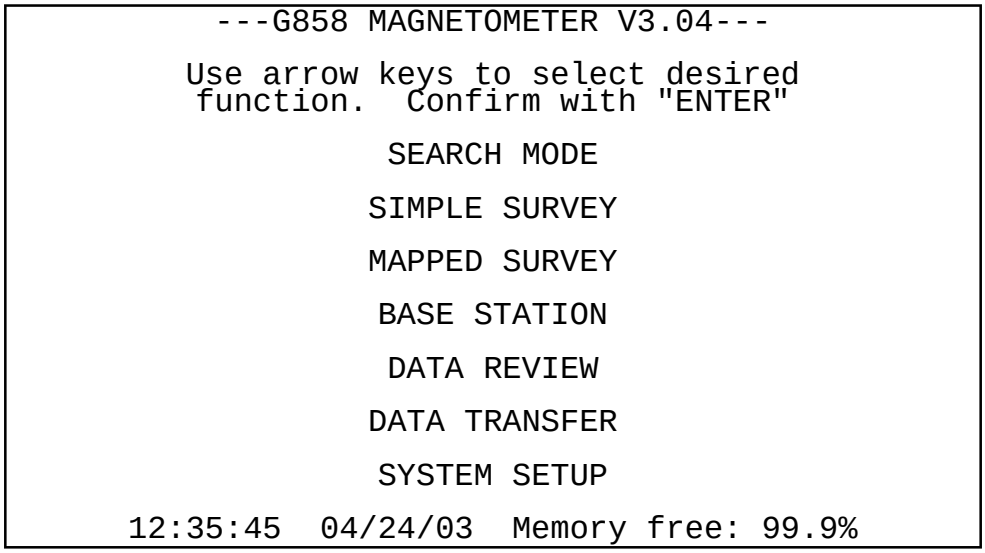
Date and Time Menu.

Enter the correct values in the numeric entry fields, then highlight SET TO THE ABOVE VALUES, and press ENTER. Hit ESC three times to return to the Main Menu.

Warming up the G-858

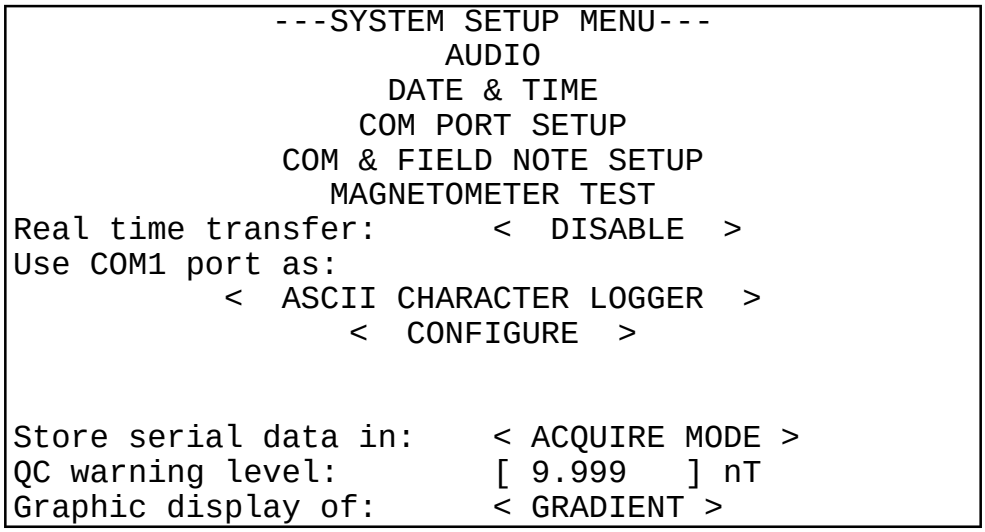
After first powering up the G-858, it may take from 5 to 15 minutes for the unit to warm up and begin operating normally, depending upon the ambient temperature. Here is a recommended procedure for starting and warming up your G-858:

From the G-858 Main Menu:



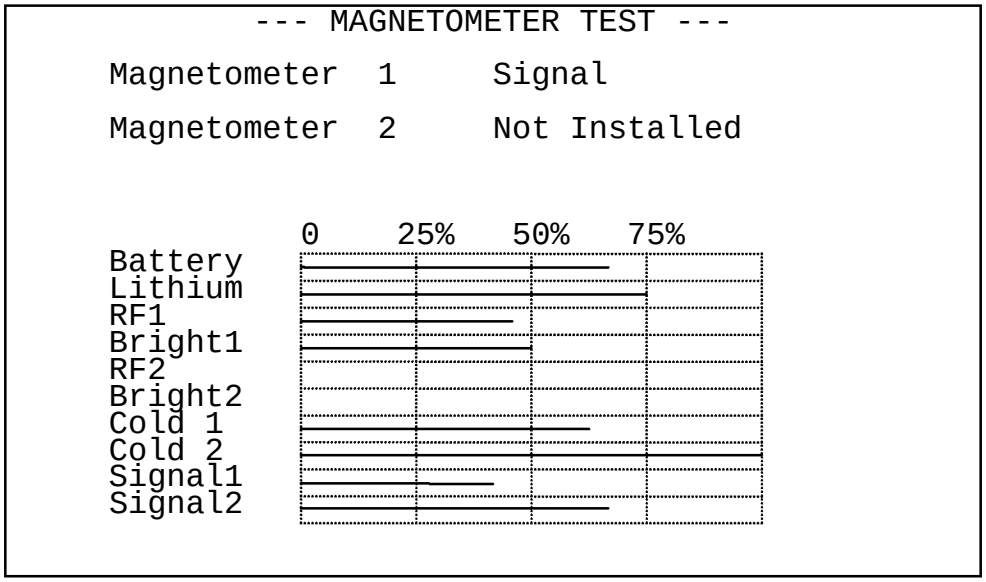
G-858 Magnetometer menu.

Highlight SYSTEM SETUP and press enter. You should see a display similar to that below:



System Setup Menu. The last line is shown only on gradiometers.

Highlight MAGNETOMETER, and press ENTER. You will now see the following display:



Magnetometer Test Display.

The exact display will differ depending upon how many sensors are installed, and how long the unit has warmed up. The unit is warmed up and operating properly when the Bright1 (and Bright2 if two sensors are installed) is maintaining a constant reading of 50%. Cold2 and Signal2 lines should be ignored if only one sensor is installed.

If no signal is indicated, it usually means that the sensor is oriented in the dead zone, or the field gradient is too high. Try orienting the sensor differently, and move it away from large ferrous metal objects. Typically, in an office or other indoor environment, gradients are too high, and the sensor signal will often not appear. See the section earlier in this chapter for more information on sensor dead zones.

From this menu, you should also check the level of the Lithium battery. If less than 65% (75% is normal) you should have the battery replaced. This should only be necessary every several years.

More information about this display is contained in Chapter 10.

Note: Occasionally, the unit may indicate a bad sensor during the warm-up period. If so, press the ESC key to stop the warning sounds, and then simply unplug the sensor and plug it back in. The sensor will then re-initialize, and should come up to the proper operating point.

You should next select SEARCH MODE from the main menu. (Press ESC 3 times to go back to the MAIN MENU). You can then observe the readings as they occur and play with different sensor orientations. The next chapter explains how to use the Search Mode.

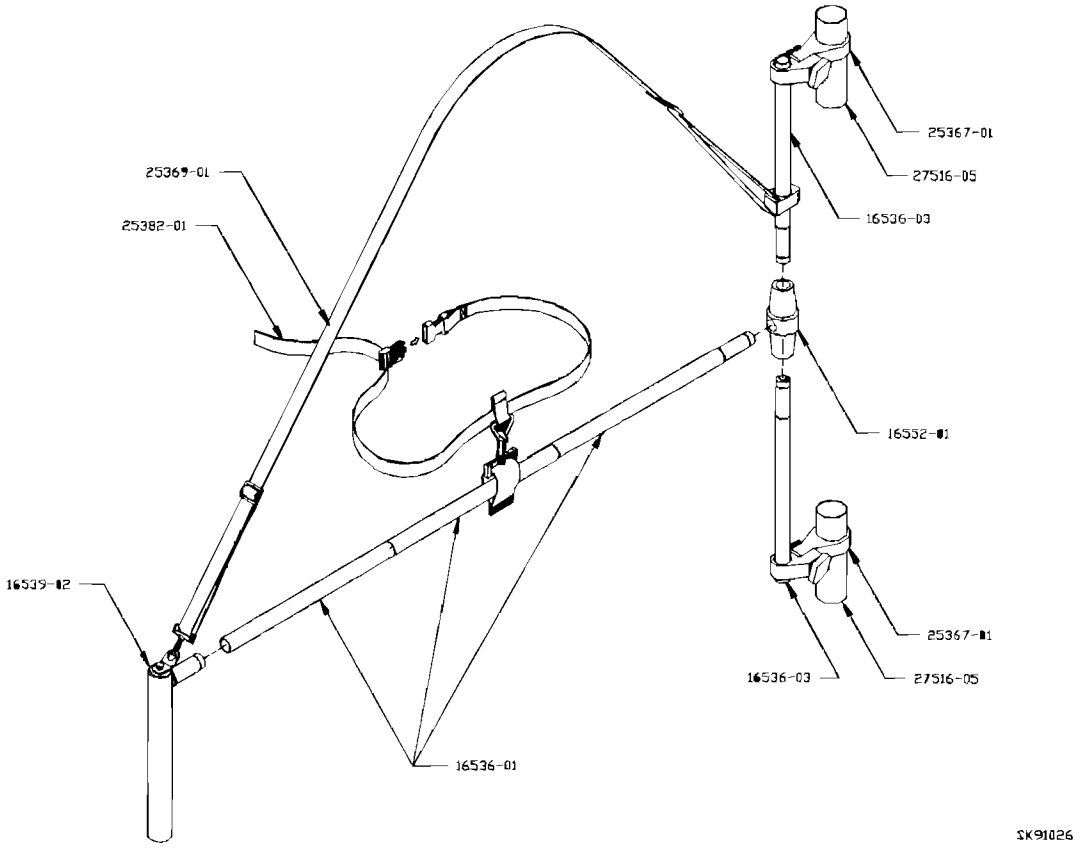
Gradiometer Operation

Operation in the gradiometer mode is essentially no different than operation in single mode. Simply plug in another sensor into the console. (Some units require a hardware upgrade to install the second channel of electronics. Please check with Geometrics.) Data will be automatically collected from both sensors.

Note: Sensor 1 should be positioned as the left sensor (from the operator's point of view) for a transverse gradient measurment, or as the top sensor for a vertical gradient measurement. The sensor 1 connector is the lower right connector on the side panel of the console.

In post-processing your data with the MagMap program, you will specify which type of gradient (horizontal or vertical) was performed.

In gradiometer operation, the sensors are positioned at the ends of a "tee", and a heavier counter weight is used. In addition, an auxiliary belt is supplied to enable some of the weight of the staff to be borne by the hips, to lighten the load on your shoulder. Having a second belt in addition to the battery belt allows more flexibility in positioning the weight of the batteries, the staff, and the console. The figure below indicates how the staff is put together.



You may choose to display either the gradient (difference between the sensors) or the value from one of the sensors on the sweep display and data review profiles. This is done from the system setup menu, which is accessed by selecting SYSTEM SETUP from the main menu.

```
              ---SYSTEM SETUP MENU---
                       AUDIO
                    DATE & TIME
                  COM PORT SETUP
               COM & FIELD NOTE SETUP
                 MAGNETOMETER TEST
Real time transfer:      <  DISABLE  >
Use COM1 port as:
           <  ASCII CHARACTER LOGGER  >
                  <  CONFIGURE  >


Store serial data in:    < ACQUIRE MODE >
QC warning level:        [ 9.999   ] nT
Graphic display of:      < GRADIENT >
```

System Setup Menu.

Highlight the “Graphic display of” item at the bottom, and press the left or right arrow key to the desired setting. When in the FIELD setting, the display will indicate the reading from the top (or left) sensor.

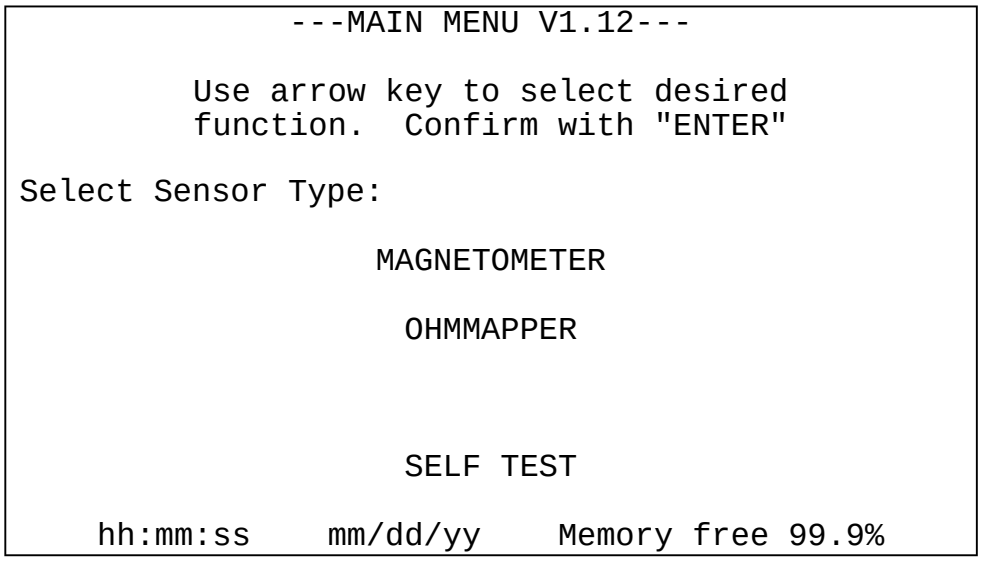
Note: Neither setting will affect the storage of data. Data from both sensors is always stored and transferred to the PC. The host software will output both the difference and each sensor reading, automatically.

To begin to explore the various modes of operation of the G-858, press the ESC key to return to the G-858 Magnetometer menu and read the chapters that follow.

```
          ---G858 MAGNETOMETER V3.04---

        Use arrow keys to select desired
         function.  Confirm with "ENTER"

                   SEARCH MODE

                  SIMPLE SURVEY

                  MAPPED SURVEY

                   BASE STATION

                   DATA REVIEW

                  DATA TRANSFER

                   SYSTEM SETUP

      12:35:45  04/24/03  Memory free: 99.9%
```

G-858 Magnetometer menu.

The G-858 also provide other Self Test functions that may be acessed. From the menu shown above press the ESC key to return to the main menu.

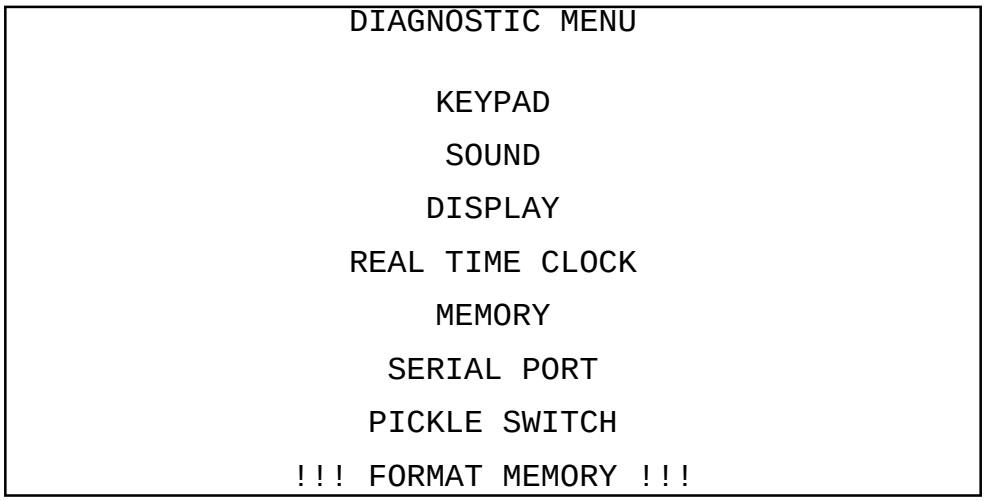


Main Menu

Use the arrow down key to select SELF TEST and press the ENTER key to see the DIAGNOSTIC MENU.

Self Test

Selecting SELF TEST from the Main Menu will display the following menu:



Keypad

This will bring up a menu for testing the keypad.

Sound

This will emit a continuous sound at maximum volume for you to test your hearing.

Display

Checks to see if the graphics mode of the display is working.

Real Time Clock

Checks the on-board real-time clock.

Memory

Checks the system memory. DO NOT DISCONNECT THE BATTERY DURING THIS TEST. Doing this will result in loss of all data stored in the instrument.

Serial Port

Checks the serial port. You must attach a loop-back cable, available from computer stores, in order to perform this test.

Pickle Switch

Tests the optional external switch.

Format Memory

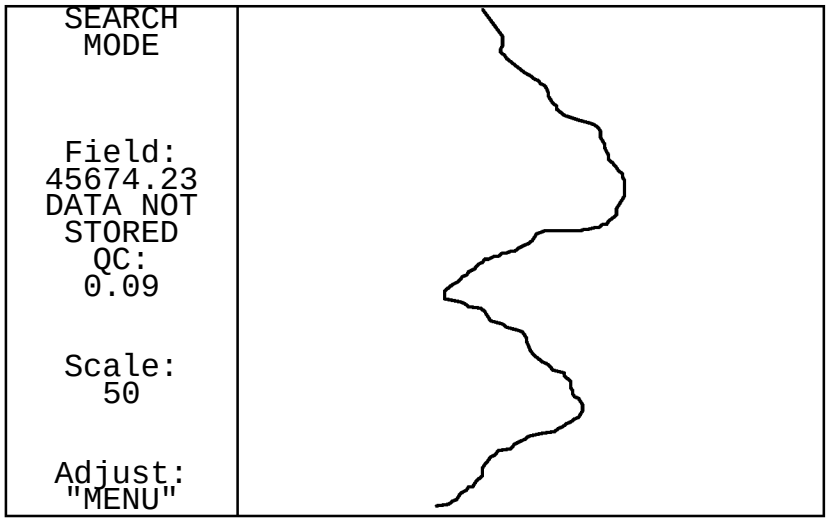
Erases the entire data memory of the G-858. All data in all files will be lost. If the system hangs up at some point, you may need to do this after power up to get the unit to behave properly.

Chapter 3: Search Mode

Search Mode

In search mode, the magnetometer operates normally, displaying data and the woowee audio tones, but data is not stored in memory. This is useful for manually identifying anomaly locations, much as with a metal detector. It is also useful for checking for proper sensor operation and ambient magnetic noise.

Select SEARCH MODE from the main menu. You should see a display similar to that below:

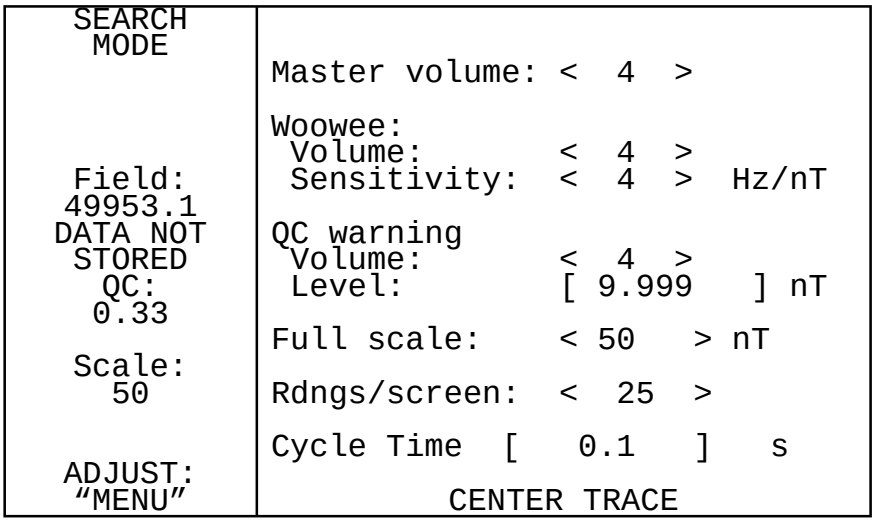


Example of Search Mode Display

Note: Data is not stored in Search Mode. This is indicated on the display, so you do not confuse it with Simple Survey.

Search Mode Adjust Menu

Pressing the MENU key will bring up the Search Mode Adjust Menu. This allows you to adjust the display and audible tones:



Search Mode Adjust Menu.

Master Volume

Adjusts the over-all volume. 1 is softest, 9 loudest.

Woowee Volume

1 is softest, 9 loudest

Woowee Sensitivity

Adjusts the amount the pitch of the woowee changes with varying field readings.

QC warning volume

1 is softest, 9 loudest

QC warning level

Sets the threshold for the QC warning to be emitted. If the QC exceeds this threshold, the warning is sounded.

Full Scale

Sets the trace width full-scale of the display.

Readings per screen

Sets the vertical scale of the trace display. Higher values means the trace moves more slowly down the screen.

CENTER TRACE

Centers the trace in the sweep display.

Pop up Menus

While in Search Mode (and the other modes as well), there are two quick pop up menus that are accessible:

Audio Key

Pressing the AUDIO key will bring up an audio adjust indicator. Then the up- and down-arrow keys will adjust the volume, while the right- and left-arrows will adjust the pitch of the woowee. The audio adjust indicator will disappear after a few seconds.

Scale Key

Pressing the SCALE key will bring up an scale adjust indicator. Then the up- and down-arrow keys will adjust the speed of the sweep (readings shown per page), while the right- and left-arrows will adjust the full scale (in nT). The scale adjust indicator will disappear after a few seconds.

Chapter 4: Simple Survey Mode

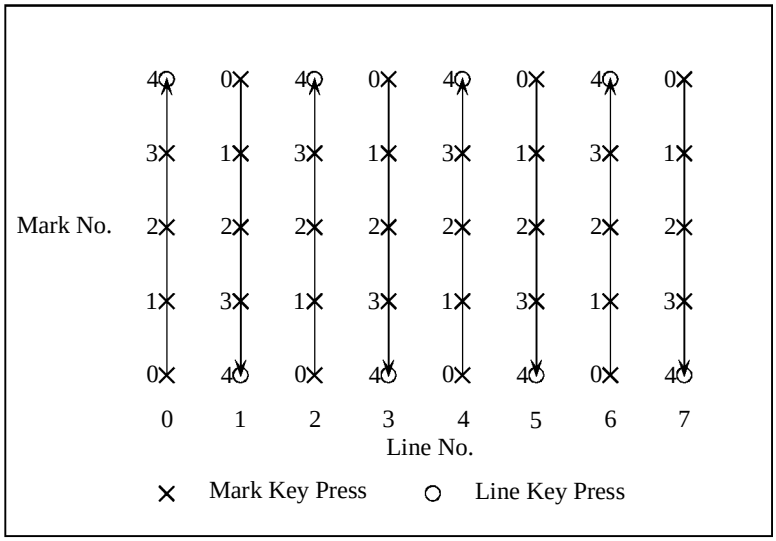
Simple Survey

Once the unit is reading properly in Search Mode, you are ready to begin your survey. If you are unfamiliar with magnetic surveys, please read Appendix 1 and the *Applications Manual for Portable Magnetometers*, shipped with your G-858.

In simple survey mode, the unit keeps track of MARK and END LINE key presses in order to locate the position of the sensor readings. Later, after downloading the data into the PC, you will use the MagMap program to attach an x and y coordinate to each reading.

Survey Overview

Typically, a survey is performed by walking up and down the survey area, surveying a series of lines, as shown below.



Simple Survey Overview

It is most convenient to survey lines walking in both directions, as shown, rather than walking back to the bottom of the map, always surveying up (either method maybe used, however). You will start at the lower left corner of the map, and walk up line 0. pressing the MARK key at each 'X'. At the end of line, press the END LINE key. You will then walk d.own line 1, and so on until the survey is finished.

Note: The line and mark numbers begin at zero. This is the most common convention, and the one adopted in the G-858. It is important to remember this, as it is sometimes easy to get confused. The survey shown above has a total of 8 lines, starting with number 0.

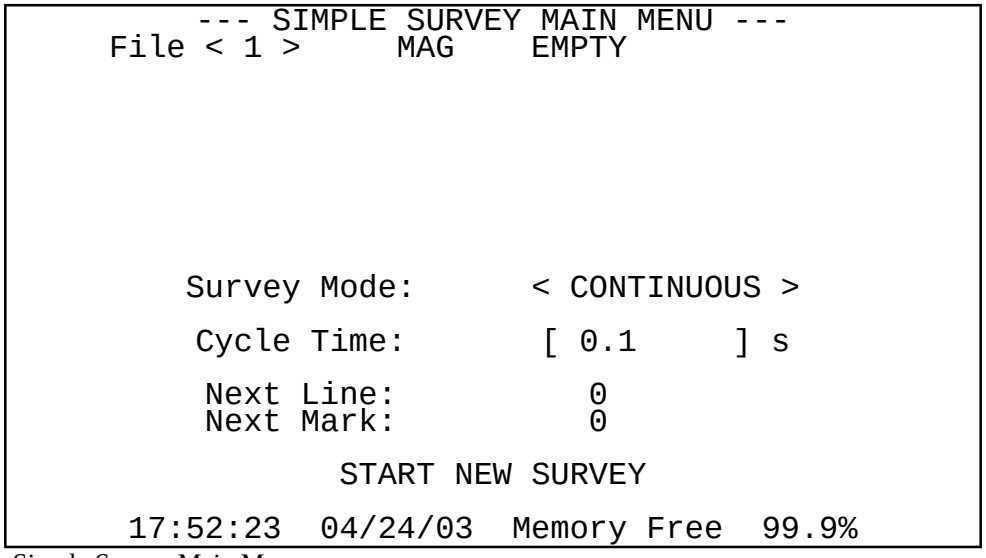
The MARK points are numbered sequentially, even in the case of a bi-directional survey, as shown in the previous figure.

MARK key presses are numbered starting from 0 at the beginning of the line. This is true whether you survey lines walking in both directions or not. The MagMap software will sort out the line direction on the PC.

If a survey is expected to last several hours or more, it is strongly recommended that you set up a second magnetometer as a base station to be used to correct for the diurnal variations in the Earth's magnetic field.

Setting up a Simple Survey

Select simple survey from the main menu, bringing up the simple survey main menu.



Simple Survey Main Menu.

If someone else has already stored some surveys, the menu may not say empty. Highlight the file number, and press the left or right arrow keys until an empty file is displayed. If all 5 files are used, you will need to erase one of them. Please check with whomever has made these surveys to make sure they have downloaded the data. Files may be erased through the DATA TRANSFER section of the Main Menu. See Data Transfer, later in this chapter.

File

File numbers from 1 through 5 may be selected. You may start a new survey from any empty file number, and may continue any Simple Survey file.

Survey Mode:

Set to CONTINUOUS for continuous data acquisition at the rate given by the cycle time, set in the field below. In discrete mode, the unit will take and store a reading at each END LINE or MARK key press.

Cycle Time

This field has two functions. In continuous mode, it sets the rate at which readings are stored. This number also sets the measurement interval. Increasing this interval will increase the resolution, up to the maximum resolution which occurs at 1.5 seconds. Numbers higher than that will increase the spacing between readings, but will not affect the resolution.

In discrete mode, this number sets the measurement interval only. Increasing this number up to 1.5 seconds will increase the resolution. Again, beyond that, the resolution will not increase.

Next Line

Next Mark

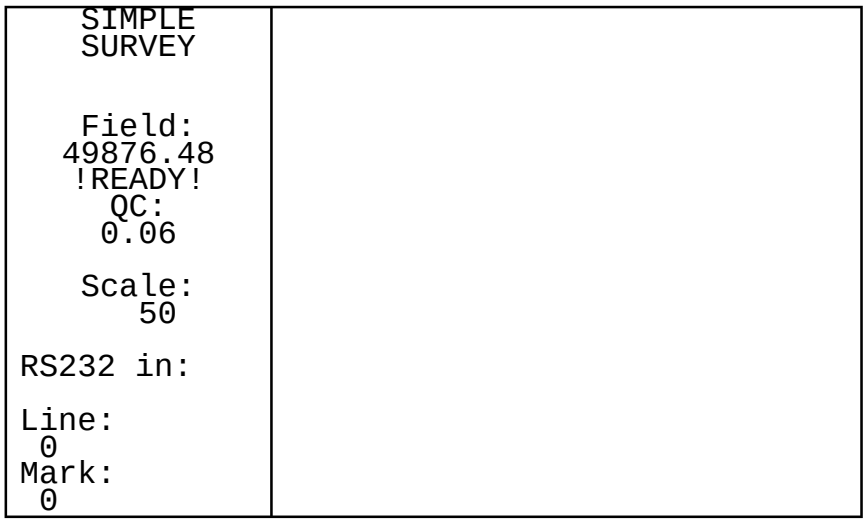
Where the unit expects you to start or continue the survey.

Note: Every new survey will begin at Line=0, Mark=0. After downloading the data into the PC, you will use the MagMap program to specify the actual starting coordinates.

If you wish to continue a previous data set, scroll the data set number to the desired set, then select CONTINUE SURVEY. Data sets for mapped surveys or base station surveys will be shown as the data set number is scrolled. However, from this menu you may not select CONTINUE SURVEY for anything other than simple surveys.

Acquiring Data

Once START NEW SURVEY or CONTINUE SURVEY has been selected, the display will change to the acquisition display.



Acquisition Display.

The items shown on the acquisition display are as follows:

Field:
Displays the magnetic field reading. If the unit has the gradiometer option, and two sensors are connected, this number may represent the gradient of the field. This is set in the Setup Menu (reached through the Main Menu).

READY
Indicates that the instrument is ready to acquire data. Data is not currently being acquired, however.

QC:
Displays a quality check indication. This value grows for rapidly varying fields. If the value exceeds a threshold (set in the system setup menu or the adjust menu) a warning sound will be heard.

Scale
Displays the full-scale width of the sweep trace on the right hand side of the display, in nT.

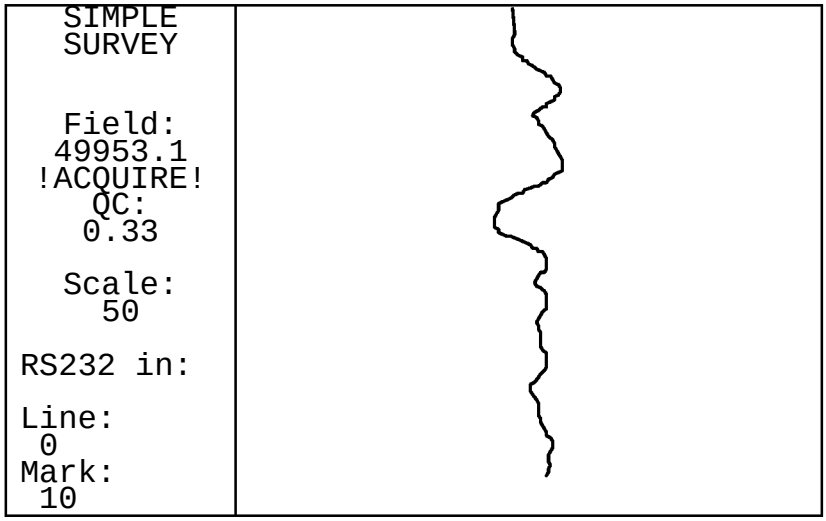
Line
Indicates the line number at which your next END LINE or MARK key press is expected.

Mark
Indicates the mark number at which your next MARK or END LINE key press is expected.

Note: The line and mark number displayed is always the location of the *next* MARK or END LINE key press.

. The unit will not be taking data yet. To start data taking, go to the starting or continuing point (indicated on the display) press the MARK key, and start walking. If you have established way points along the profile, press the MARK key at each way point. Press END LINE when you reach the end of a survey line. Press PAUSE if you want to stop recording, and PAUSE again to resume recording (the PAUSE key is effective only in continuous mode). The data display will indicate the reading with a trace display.

Note: The MARK key performs two operations. It starts the storage of data (at the beginning of a line) and logs positions into memory.



Acquisition Display with Reading Trace.

When you reach the end of each line, press the END LINE key. Upon this action, the unit will stop logging data and display a summary of the previous line:

YOU HAVE JUST REACHED THE END OF LINE.
YOU ARE CURRENTLY AT:
LINE: 0
MARK: 10

PRESS ANY KEY TO CLEAR THIS MESSAGE

THEN PRESS "MARK" TO START NEXT LINE

OR

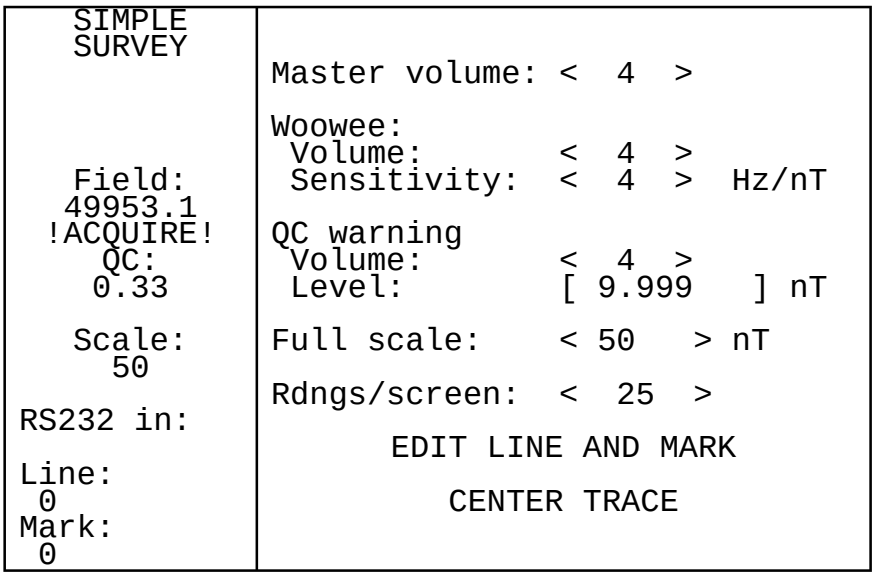
PRESS "MENU" AND SELECT
"EDIT LINE AND MARK"
FOR EDITING

To start the next line, you must first press any key to clear this dialog box, then press MARK as you start walking up the next line. We encourage you to look at this line summary between lines, to make sure you are where the unit thinks you are, and the last line has the right number of mark key presses. If there is a problem at this point, you may edit the most recently taken data. You are not able to edit any except the most recently acquired data.

Note: Don't forget the key press necessary to clear the dialog box. The END LINE key is handy for this since it was the last key pressed. If you forget to clear the dialog box, the next MARK key press will not start data acquisition (it will only clear the dialog box).

Adjust Menu

Pressing the MENU key from the Acquisition Display will bring up the adjust menu. This allows you to adjust the display and audible tones, and to enter the data editing menu.



Simple Survey Adjust Menu.

Master Volume

Adjusts the over-all volume. 1 is softest, 9 loudest.

Woowee Volume

1 is softest, 9 loudest

Woowee Sensitivity

Adjusts the amount the pitch of the woowee changes with varying field readings.

QC warning volume

1 is softest, 9 loudest

QC warning level

Sets the threshold for the QC warning to be emitted. If the QC exceeds this threshold, the warning is sounded.

Full Scale

Sets the trace width full-scale of the display.

Readings per screen

Sets the vertical scale of the trace display. Higher values means the trace moves more slowly down the screen.

EDIT LINE AND MARK

Opens the data editing menu. See detail below.

CENTER TRACE

Centers the trace in the sweep display.

Pop up Menus

From the acquisition display, there are two quick pop up menus that are accessible:

Audio Key

Pressing the audio key will bring up an audio adjust indicator. Then the up and down keys will adjust the volume, while the right and left arrows will adjust the pitch of the woowee. The audio adjust indicator will disappear after a few seconds.

Scale Key

Pressing the scale key will bring up an scale adjust indicator. Then the up and down keys will adjust the speed of the sweep (readings shown per page), while the right and left arrows will adjust the full scale (in nT). The scale adjust indicator will disappear after a few seconds.

Pausing

Pressing the PAUSE key while acquiring data will temporarily stop data acquisition. At this point, you may do any of the following:

Press PAUSE. This will re-start the acquisition process.

Press MARK. This will enter the current position. Do this only if you are currently at one of your way points. Only one MARK key press is allowed. The instrument will stay in pause mode.

Press END LINE. This will enter the END LINE position. Do this only if you are at the end of the line. The instrument will switch out of pause mode, and into the normal between-line state. Next, press the MARK key to start taking data.

Editing Data

Selecting EDIT LINE AND MARK from the adjust menu (above) will show the edit menu.

```
SIMPLE SURVEY EDIT MENU

You are currently going to:
        Line:   4
        Mark:   1


GO BACK TO LAST POSITION:
        Line:   4
        Mark:   0

DELETE LINE:
        Line:  4


RETURN TO SURVEY
```

Simple Survey Edit Menu.

From this menu, you may delete the most recently acquired data.
The meanings of the menu items are:

GO BACK TO LAST POSITION

Selecting this will delete data to the last MARK or END LINE key press.

DELETE LINE

Selecting this will delete the most recent line. If you are in the middle of a line, the current line will be deleted.

Examples - Recovering From Common Mistakes:

Mistakenly pressing MARK instead of END LINE at the end of a line.

This is a fairly common occurrence, and easily fixed. First, press PAUSE to halt the data acquisition. Then press ESC to close the dialog box. Press MENU, then highlight EDIT LINE AND MARK and press ENTER to bring up the Edit Menu, shown above. Highlight GO BACK TO LAST POSITION and press ENTER. Next, press ESC twice, to show the Acquisition Display. Then press END LINE. You have now corrected your mistake.

Sometimes, after pressing the MARK key at the end of a line, you might press the END LINE key instead of PAUSE, as mentioned above. In this case, from the Edit menu you should highlight GO BACK TO LAST POSITION and press ENTER *twice*. The first press takes you back to the position entered by the END LINE key press (which is one mark spacing past where you want it to be). The second press takes you back to where you actually want the end of line to be. Then, you press ESC twices, and press END LINE.

Mistakenly pressing END LINE instead of MARK in the middle of a line.

After pressing END LINE in the middle of a line, press ESC to clear the dialog box. Then, press MENU, highlight EDIT LINE AND MARK and press ENTER. Next, highlight GO BACK TO LAST POSITION and press ENTER. Press ESC twice to bring up the Acquisition Display.

You are now ready to continue the line where you were when you originally pressed the END LINE key. Position the sensor at the proper location, press MARK, and start walking. You are now taking data.

Realizing the data for your current line is erroneous.

Another common reason for editing data is if you realize a line has incorrect data, often either due to missing a MARK key press at a fiducial point, or walking off course. If this occurs, simply press the END LINE key, enter the edit menu, highlight DELETE LINE and press ENTER. Then select RETURN TO SURVEY (or press ESC), walk back to the beginning of the line, make sure the next line number displayed is correct, press the MARK key and begin the line over again.

Note: From the edit menu, you may delete as many lines or segments as you wish, all the way back to the beginning of the survey.

Summary

Data editing in simple survey is somewhat like pressing backspace on a computer. You can delete data and positions going backward from the most recent key presses. Note that this is the only way to alter the counting of marks and lines.

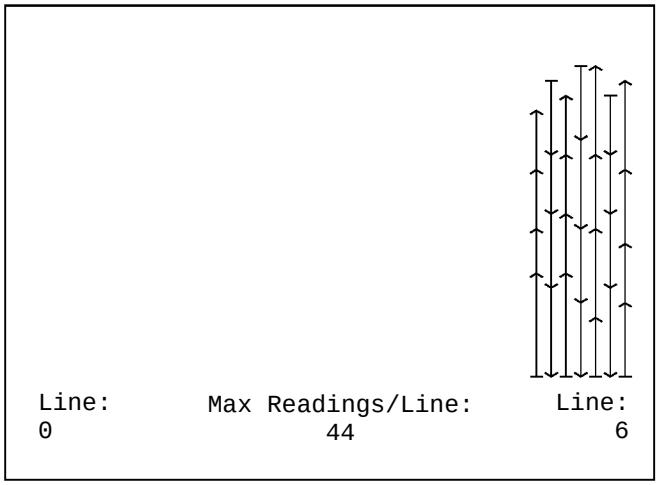
After making data edits, it is very important to make sure the current line and mark number are where you intend to take data. It is strongly recommended that you look at the Map display after editing data. See the next section on viewing data.

Viewing Data

Pressing the MAP or CHART key from the Acquisition Display will bring up a representation of the data acquired. These keys may be pressed at any time. The unit will pause while you look at the display.

Map Display

On the map display, each mark is represented by an arrow in the default direction. The distance between marks is proportional to the number of readings taken. Thus, if you are doing a bi-directional survey, and are walking at a steady pace, this display will correspond to a physical map. Otherwise, it gives an indication of the number of marks in each line and the number of readings taken between marks. The map display, after 7 lines of data have been taken, is shown below:



Map Display in Simple Survey Mode

Data is shifted all the way to the right, with the oldest data shown on the left. The number at the lower left indicates the number of the left-most line, while the right hand number indicates the right-most line on the display. The arrow keys may be used to scroll the display, if necessary.

Pressing ESC will exit the map display.

Chart Display

You may review the data readings as profiles by pressing the CHART key. You may scroll both the map and charts by hitting the left and right arrow keys. If you were logging data when you pressed the MAP or CHART keys, the unit will enter the pause mode while it is displaying the map or profiles. To restart data acquisition, press ESC, then PAUSE. The chart display is shown below:

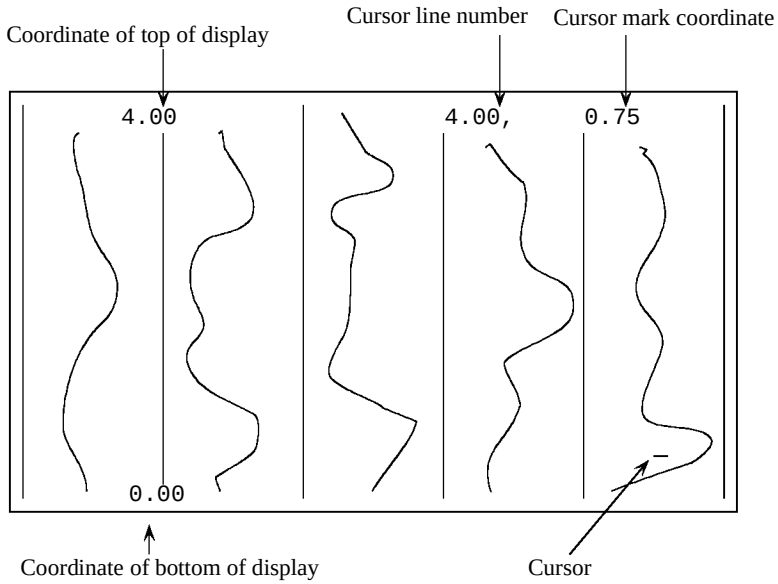


Chart Display in Simple Survey.

On the chart, coordinates are in units of marks. For example, a y-value of 3.5 indicates half way in between mark 3 and mark 4.

Chapter 5: Mapped Survey.

Introduction

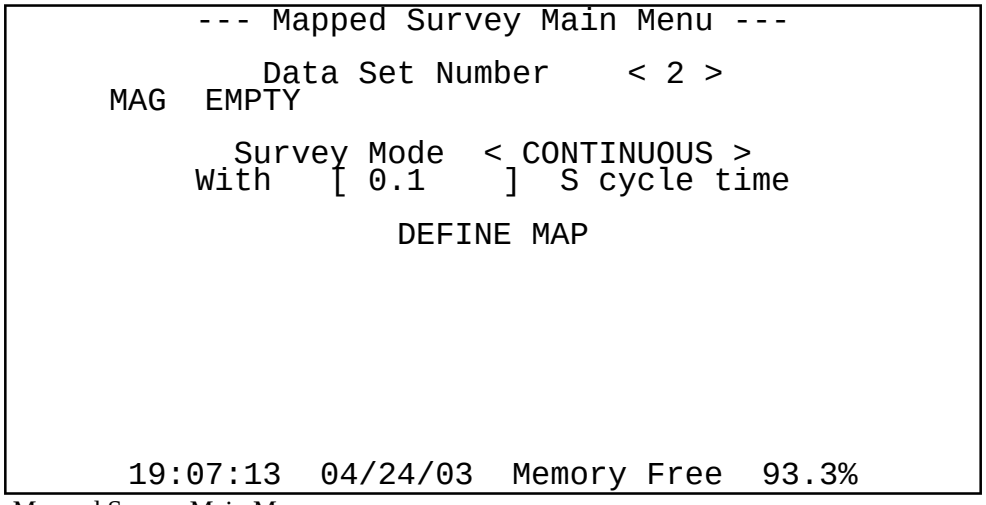
Mapped survey allows you to better specify and visualize the survey area than simple survey, and to move around within the area in a non-continuous fashion. Using the arrow keys, you may position the cursor anywhere within the map, and acquire data. Default cursor movements are programmed into the unit, so if you follow a normal serpentine path across the survey area, you may simply press the MARK and END LINE keys as if you were doing a simple survey.

Mapped mode allows you to

- Define a rectangular survey area with pre-defined fiducial, or mark, points on a regular grid.
- Take data in a uni-directional, or bi-directional default pattern.
- Move to any arbitrary position within the survey area to take data.
- Leave gaps in the survey where positions are inaccessible.
- Observe on-screen where all data points have been logged.

Setting up the survey

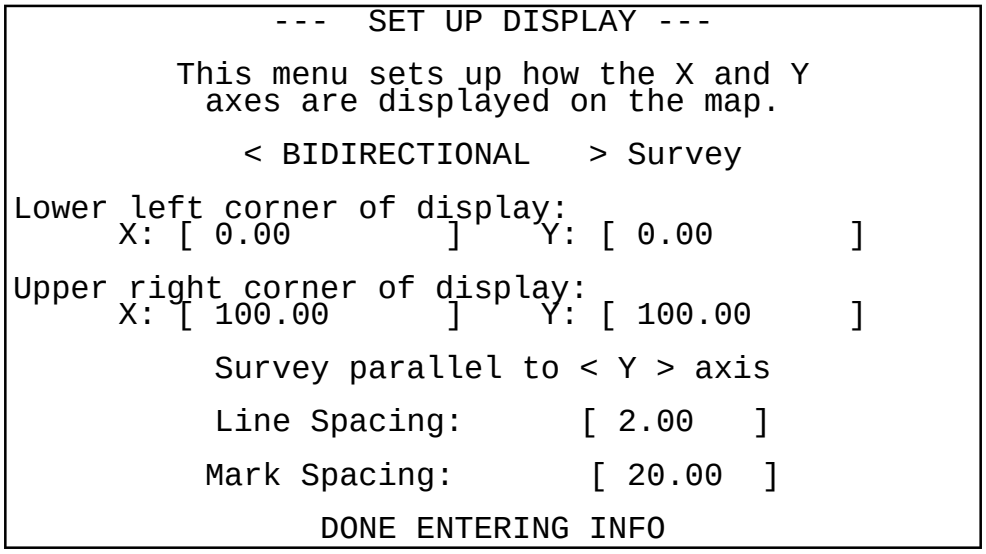
From the main menu, select MAPPED SURVEY.



Mapped Survey Main Menu

To start a new data set, press the right or left arrow keys until an empty data set is indicated. The Survey Mode may be set to continuous or discrete. In discrete mode, a reading will be taken only upon the operator pressing the MARK or END LINE keys. In continuous mode, readings are taken at intervals specified by the cycle time. The cycle time may be set from 0.1 to 6553.4 seconds in 0.1 second increments. Adjust the parameters shown, if necessary, then select DEFINE MAP. This brings up the set up display menu.

Defining the Survey Area



Set Up Display Menu

The actions of the various fields areas follows:

Bi-directional or uni-directional survey

This field describes whether you will take data walking both up and down lines or walking up the lines only.

Lower left corner

Upper right corner

Here, you must describe the coordinates of the survey area by entering the lower left and upper right extents of the displayed area. If the area is not a rectangular shape, define a bounding rectangle containing the survey site. You may use any units you like.

There are several things you must keep in mind when deciding how to define the survey, and how you will be walking to cover the area. First of all, survey lines are assumed to be shown vertically on the display. This makes it easier to visualize where you are when you are standing at the beginning of a survey line looking towards the end of the line.

Secondly, the unit assumes that you will be surveying lines from left to right across the display. In other words, when the END LINE key is pressed the cursor will move to the next line to the right on the display.

The map height must be an integral number of mark spacings. During the survey, you may manually enter positions at ends of lines which do not reach to the next fiducial mark. See the section "Manually Entering a Position," later in this chapter.

Note: Remember that you are defining the way the coordinates are viewed on the display of the G-858. See the later section "Defining a Physical Area" for more details on how to define your survey.

Survey parallel to X or Y axis

This action defines which axis you want displayed vertically on the screen. This is the axis your lines will be parallel to.

Line spacing

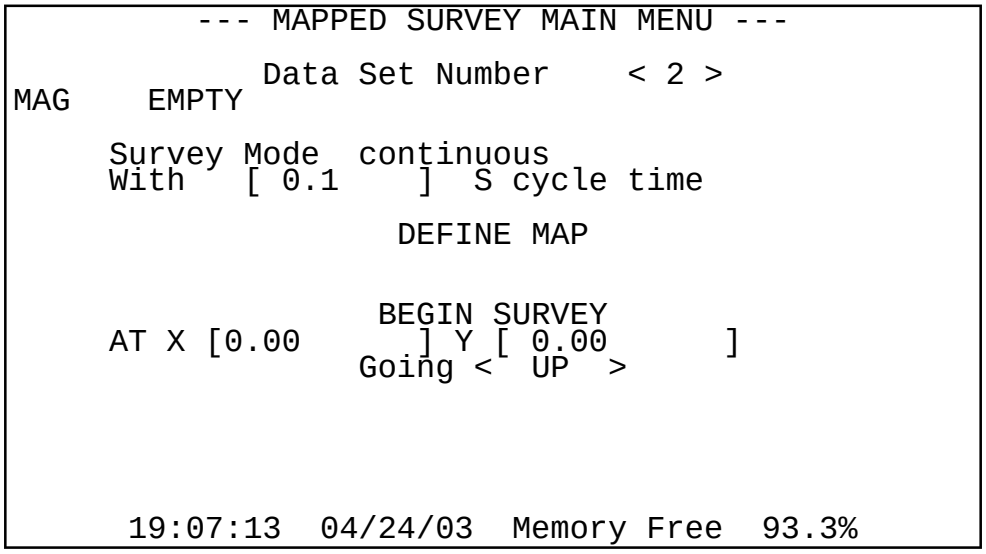
Mark spacing

These items define the distance between lines or marks.

Enter the desired parameters in the set up display menu, then select DONE ENTERING INFO, or press ESC.

Note: If the unit beeps and displays a warning dialog box, you have entered inconsistent information. Usually, this means that the chosen survey direction (x- or y-axis) is not vertical on the display screen. Either change the survey direction or the lower left and/or upper right values for the display. See Defining a Physical Area for more information.

After the G-858 accepts the values you have entered, the mapped survey main menu will reappear, with some new options:



Now you can manually adjust the starting point, if desired. The default starting point will be the lower left corner, and the unit will assume you will be initially walking up the display. You may adjust the starting point and direction, if desired. Then select BEGIN SURVEY.

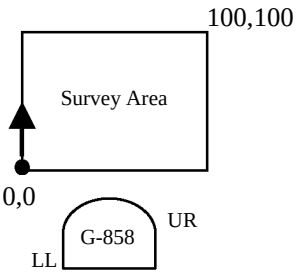
Continuing a previous mapped survey is done in a similar way. Scroll to the desired data set number, then select CONTINUE SURVEY.

Note: You may redefine the map region for a survey that has data in it. This is done simply by selecting DEFINE MAP from the main map menu, and modifying the data. This allows an enormous amount of flexibility in taking a survey. Please see the section “Multiple Grid Surveys” below.

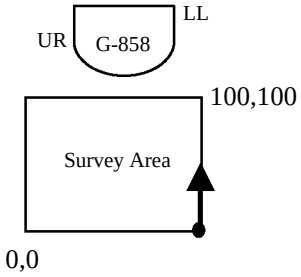
The following provided examples of how to set up the G-858 for varios surveys.

MAGMAPPER MAPPED SURVEY MODE - PARALLES TO Y AXIS

All coordinates are defined as (x,y)



LL(0,0)	Y axis
UR(100,100)	Start UP at (0,0)



LL(100,100)	Y axis
UR(0,0)	Start DOWN at (100,0)

NOTE: Though you are surveying the area from right to left, the map appears left to right

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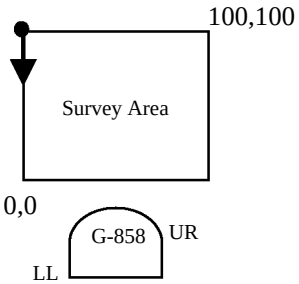
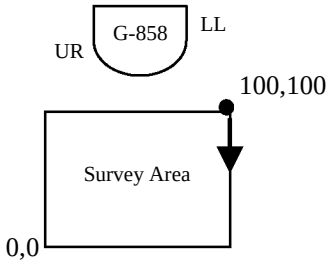


LL(0,0)	Y axis
UR(100,100)	Start DOWN at (0,100)

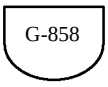


LL(100,100)	Y axis
UR(0,0)	Start UP at (100,100)

NOTES: **UR** is Upper Right, **LL** is Lower Left.

All surveys assume 100 by 100 units. Any rectangular dimension is acceptable.

 Represents the start and direction for the first line.

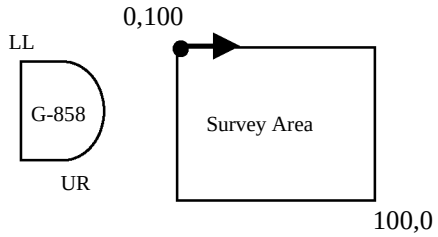


Represents the G-858 Console orientation.

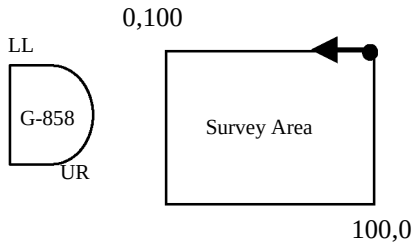
All above Mapped surveys will import into MagMap 2000 and result in correctly located data.

MAGMAPPER MAPPED SURVEY MODE - PARALLEL TO X AXIS

All coordinates are defined as (x,y)

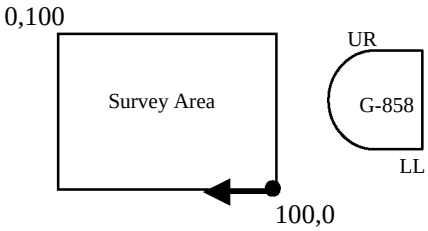


LL(0,100)	X axis
UR(100,0)	Start UP at (0,100)

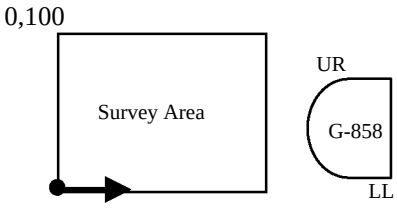


LL(0,100)	X axis
UR(100,0)	Start DOWN at (100,100)
NOT VALID FOR UNIDIRECTIONAL	

NOTE: Though you are surveying the area from right to left, the map appears left to right on the display.



LL(100,0)	X axis
UR(0,100)	Start UP at (100,0)

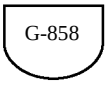


LL(100,0)	X axis
UR(0,100)	Start DOWN at (0,0)
NOT VALID FOR UNIDIRECTIONAL	

NOTES: **UR** is Upper Right, **LL** is Lower Left.

All surveys assume 100 by 100 units. Any rectangular dimension is acceptable.

 Represents the start and direction for the first line.

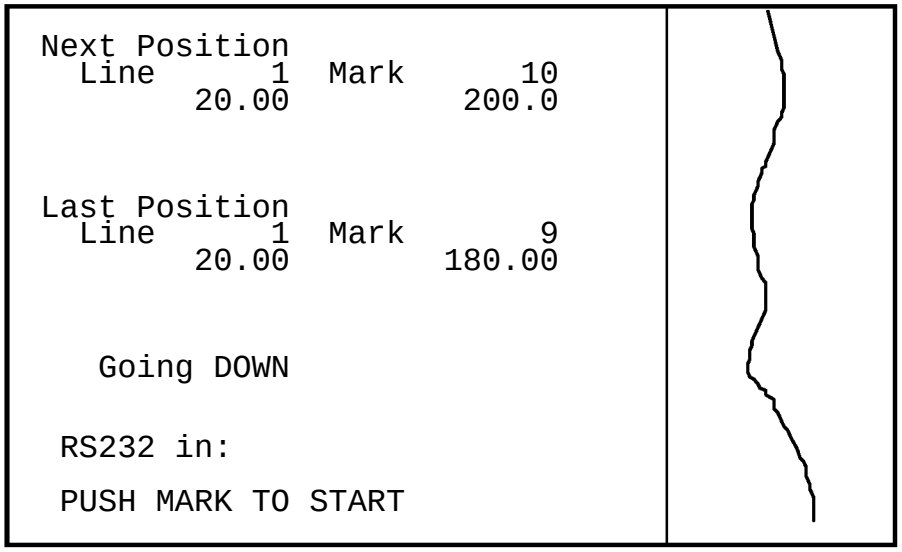


Represents the G-858 Console orientation

All above Mapped surveys will import into MagMap 200 and result in correctly located data.

Acquiring Data

Either beginning a new survey or continuing an old one will bring up the map acquisition display.



Data Display Screen

Just as in simple survey, data acquisition is started upon the operator pressing the MARK key. Acquisition will stop when the END LINE key is pressed. Position events will be stored when the MARK key is pressed during data acquisition. The PAUSE key will temporarily halt acquisition; pressing it a second time will re-start acquisition.

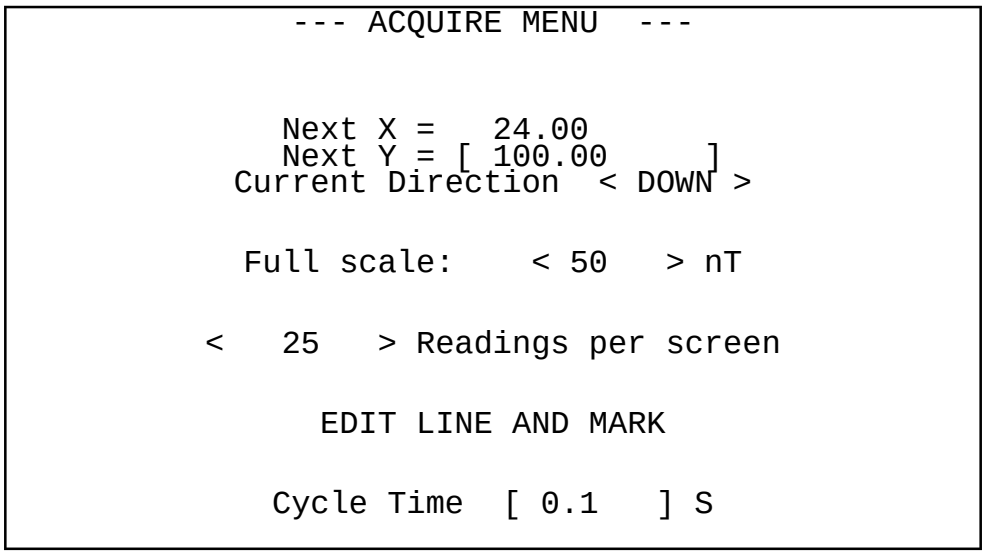
The top line of the display shows the position where you should next press the MARK or END LINE key. This should, of course, be the position you are walking toward. Below this line is shown the position of the last position event stored.

See the Advanced Features section later in this chapter for more information on specifying your position.

Note: From this display, you may press the MENU key to bring up the acquire menu, the MAP key to bring up the map display , or the CHART key to bring up the data review menu. These functions are described next.

Acquire Menu

Pressing the MENU key will bring up the acquire menu.



Next X
Next Y

You may change position along the line you are on. Depending on the direction of your survey, you will be allowed to enter a number into one of these two fields. This is very useful when your path is blocked. See the later section "Advanced Features" for more information on using this feature.

If you are between lines, you will be allowed to adjust both of these numbers. You cannot, however, enter a line position which isn't on the regular grid. To do that, you must re-define the grid. See the section on Multi-Grid Surveys.

Note: You may also change the next position by pressing the arrow keys directly from the acquisition display after an END LINE key press.

Current Direction

You may toggle between up and down.

Full scale

The scale width of the sweep display, in nT.

Readings per screen

The vertical scale, or sweep rate on the display.

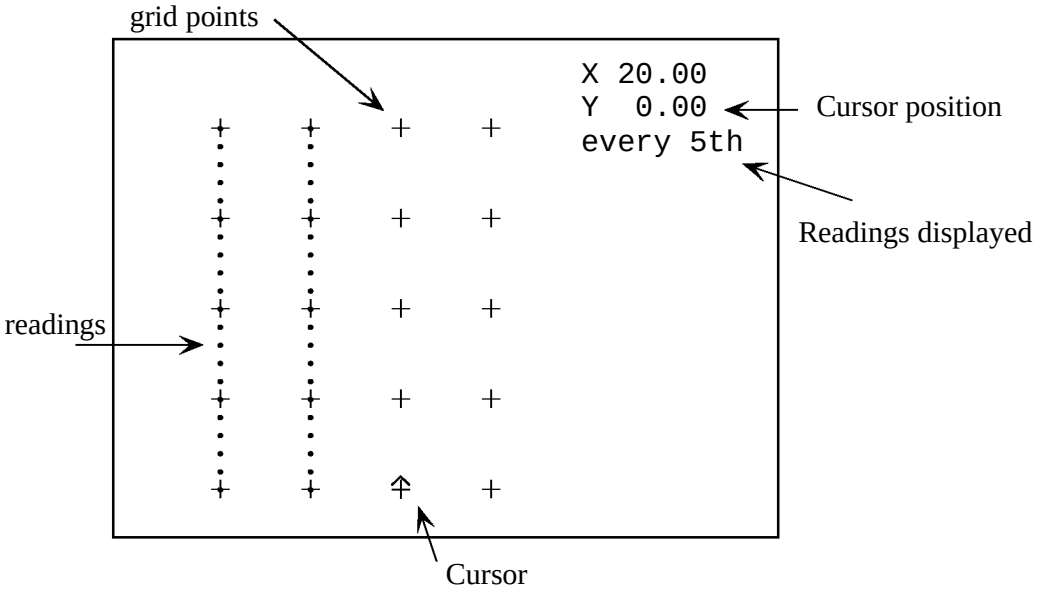
EDIT LINE AND MARK

Brings up the editing menu, see below.

Pressing ESC will return the unit to the acquisition display.

Displaying the Map

The map is displayed by pressing the MAP (.) key from the data display screen:



Map Display. Map is shown after two lines of data have been taken.

Note: To restart data acquisition, first press ESC to clear the map. Then press the MARK key.

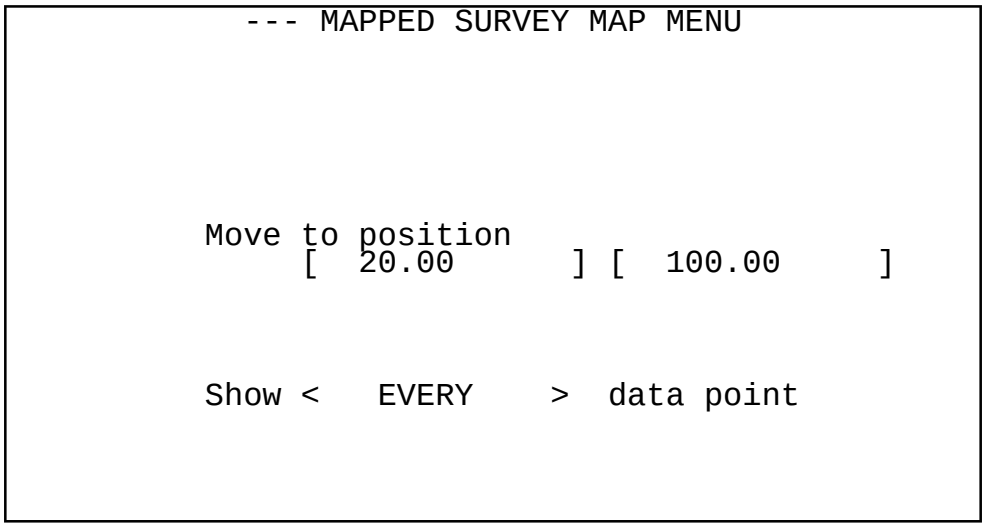
Some care must be taken in orienting the map display with the real world. On the display, the line direction is always up and down. The survey is also assumed to start at the left side of the display. Each time the MARK or END LINE key is pressed, the position is automatically updated on the map, according to whether you have selected a unidirectional or bi-directional survey. The position indicated is where the unit thinks you should be walking toward (where you will next press the END LINE or MARK keys). You may change this to any other fiducial mark by pressing the cursor keys to manually change position.

The baseline of the survey is displayed along the bottom. This is assumed to be a straight line. The edge opposite the baseline may be a more arbitrary shape within the rectangle you specified. This is done by manually entering and changing positions when you are starting or stopping a line at a position other than the back edge of the rectangular map display.

Note: After positioning the cursor, you must make sure it is pointing in the direction you want to go. Pressing "2" will point the cursor upward, and "8" will point the cursor down.

Map Menu

From the map, the MENU key brings up the Mapped Survey Map Menu:



Mapped Survey Map Menu

Move to position

This allows you to position the cursor by entering a position.

Show data point

It also allows you to reduce the number of data points plotted, to speed up the drawing process.

Pressing ESC will return the unit to the map display.

Viewing Data

Data profiles may be reviewed by pressing the CHART (-) key. The arrow keys will scroll through the data. Pressing the SCALE or MENU keys will allow you to adjust the scale.

Each line is plotted in its own lane. Values "wrap around" inside the lane. The scale may be set by pressing the scale key, or by pressing menu and bringing up the Chart adjust menu.

The chart display is shown below.

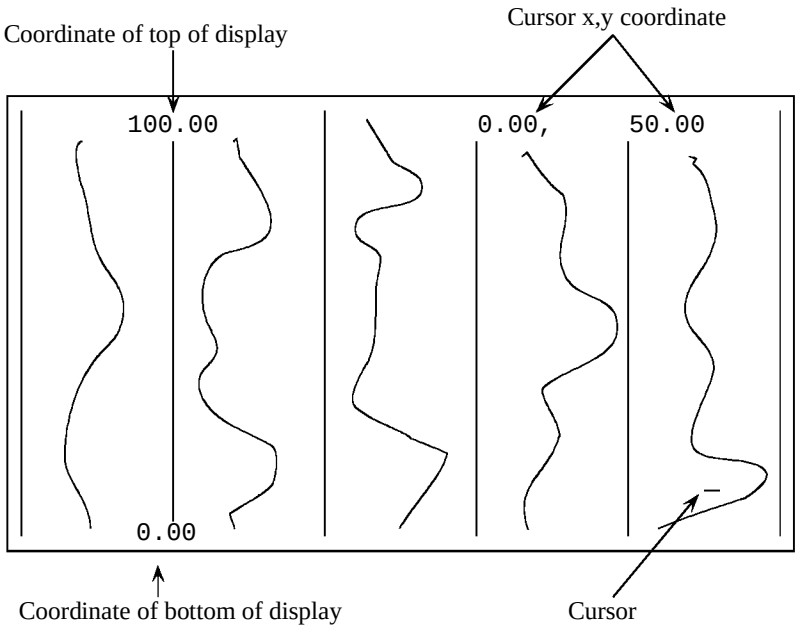
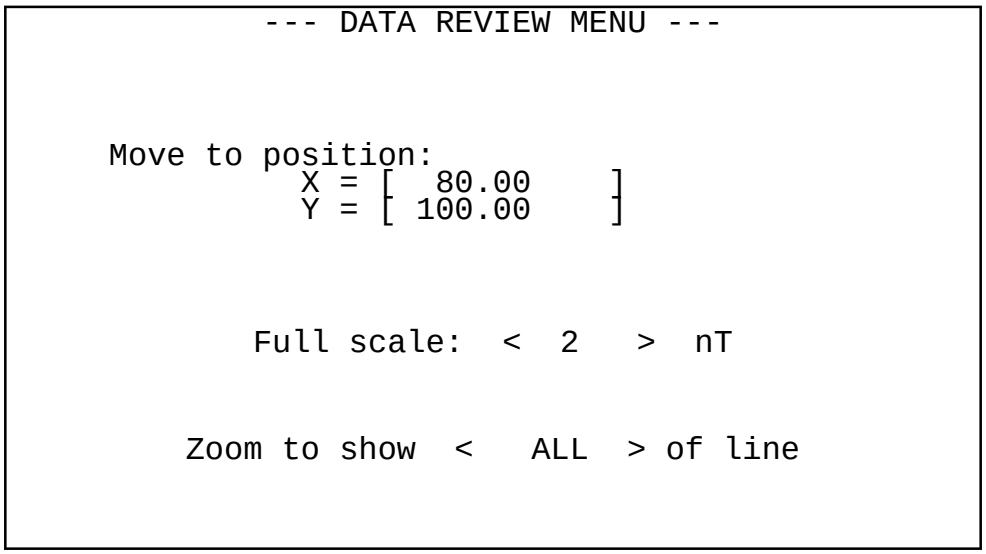


Chart Display for Mapped Survey.

Pressing the MENU key will bring up the data review menu:



Move to position

This will jump the cursor to a particular position, and scroll the data to that point. This is useful to rapidly page back to a particular point, without having to scroll through the entire file.

Full scale:

Set the full scale of each lane, in nT.

Zoom to show portion of line

Sets the vertical scale of the display.

Editing Data

Introduction

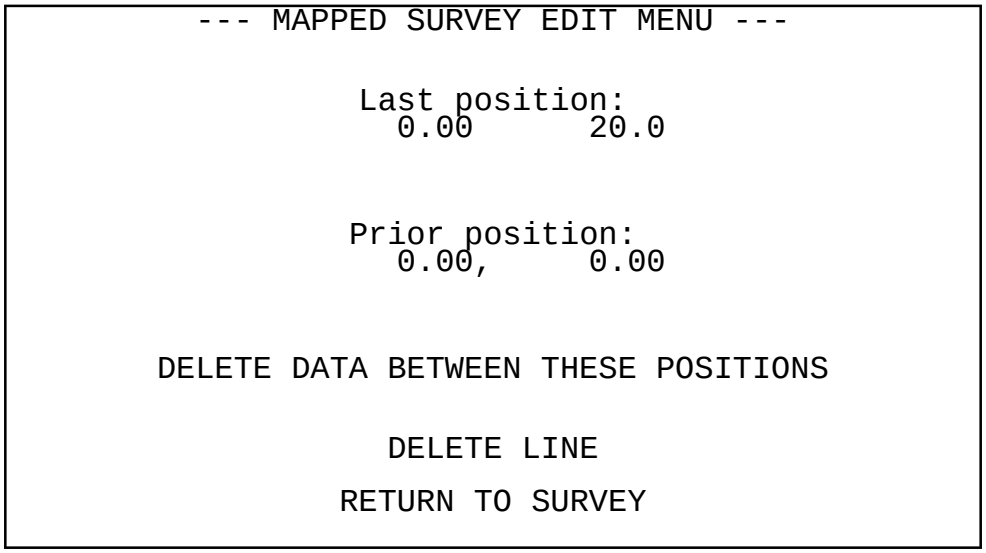
Data editing may be done in two ways. The most-recently taken data may be deleted and retaken, or you may simply retake data from anywhere within the survey. If data has been taken from overlapping locations, the MagMap software will allow you to select which set of data you want. Doing the editing on the PC, however, is an involved process. It is much easier to delete data and retake it on the spot.

Data editing in Mapped Survey is somewhat different from Simple Survey. In Mapped Survey, you have much more flexibility in positioning the cursor where you want when you are finished editing. Thus, if the default position of the cursor is not what you want, you may simply use the map and cursor movement functions to reposition it. You do not need to press the END LINE key, for example, to indicate an end of line. Simply reposition the cursor at the next line.

Also, remember to use the map make sure you deleted the data you intended to. To move from the editing menu to the map, press ESC twice, then MAP. To go back to the editing menu from the map, press ESC, MENU, then highlight EDIT LINE AND MARK (it probably will be highlighted already) and press ENTER.

Procedures

The data editing menu is reached from the acquire adjust menu. From the Acquisition Display, press MENU, then select EDIT LINE AND MARK.



Mapped Survey Edit Menu

DELETE DATA BETWEEN THESE POSITIONS

This function deletes data back to the prior mark. You will then be positioned at that previous mark.

DELETE LINE

This will delete an entire line of data. It will delete the line you are currently on, or, if the current line has no data in it, it will delete the previous line.

Examples - Recovering From Common Mistakes:

Mistakenly pressing MARK instead of END LINE at the end of a line.

First, press END LINE to halt the data acquisition. Press MENU, then highlight EDIT LINE AND MARK and press ENTER to bring up the Edit menu, shown above. Highlight DELETE BETWEEN THESE TWO POSITIONS and press ENTER. Finally, press ESC twice to return to the Acquisition Display. Then press MAP to review where data is still stored on the system, and to make sure the cursor is positioned correctly. You may need to use the arrow keys to place the cursor at the beginning of the desired line.

Mistakenly pressing END LINE instead of MARK in the middle of a line.

This case actually does not require any data or positions to be deleted. In mapped mode, all that is necessary is that you properly re-position the cursor and continue taking data. After accidentally pressing the END LINE key, press MAP to bring up the Map Display. Then, use the arrow keys to position the cursor at the mark position where you pressed the END LINE key. This position will be at the exact end of the last data segment. Next, press ESC twice to move to the Acquisition Display. Now, walk back to where you pressed the END LINE key. Press MARK and start walking. Continue the line normally.

Summary

Data editing in mapped mode is somewhat different than in simple survey mode. In mapped mode, you should visualize the survey area using the map, delete line segments or lines, then reposition the cursor where you want to go next.

To move from the Edit Menu to the Map Display, press ESC twice, then MAP. To go back to the Edit Manu, press ESC, then MENU, make sure EDIT LINE AND MARK is highlighted (it should be) and press ENTER.

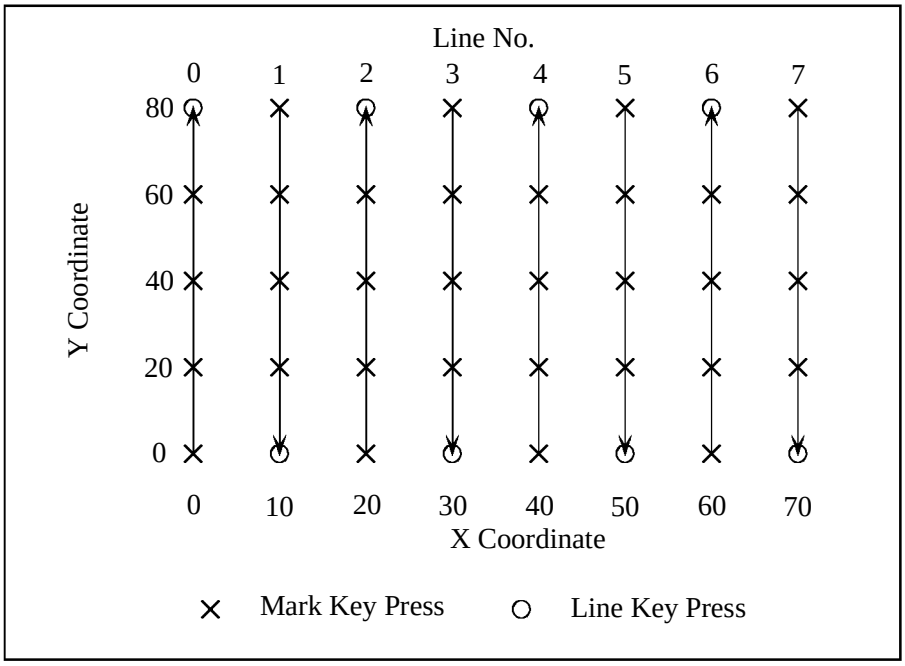
Note: It is strongly suggested that after each segment or line is deleted you bring up the map to see where you now are. Also, don't forget to check to see where the cursor has been positioned, and its direction, after the deletions are finished.

Defining a Physical Area

In the explanation above, we touched only very briefly on defining the map. This section will more clearly explain how to define the map display so that it corresponds to the mental picture you have of the actual survey site.

Normal Orientation

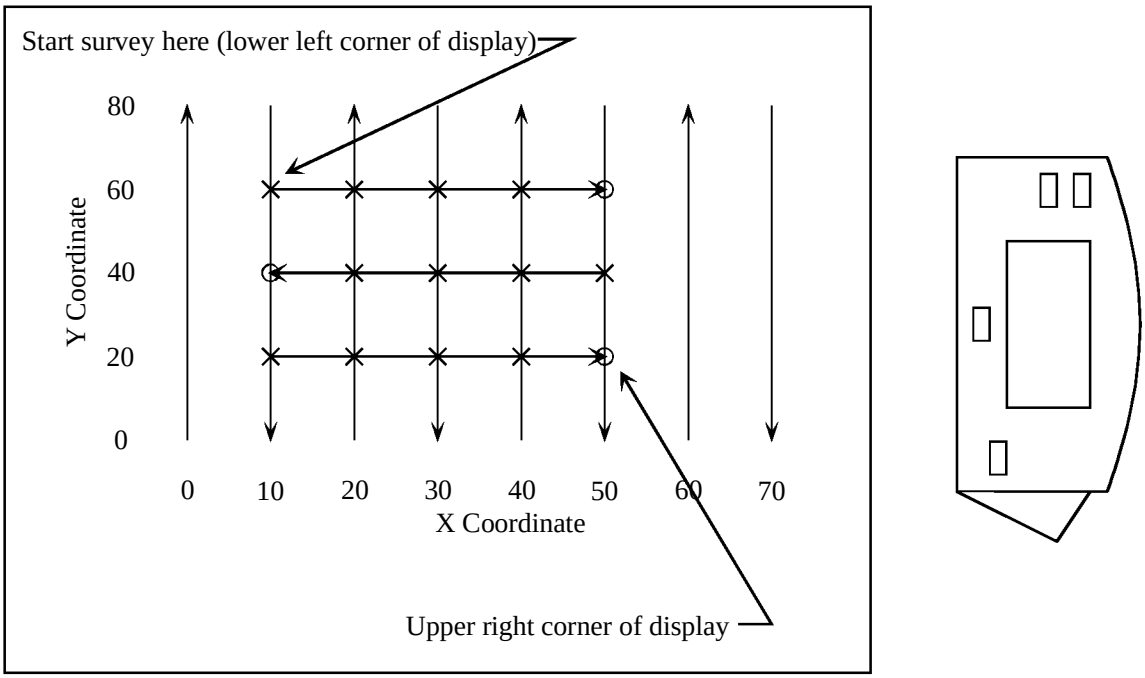
The easiest way to keep the coordinate system clear is to define the Y axis to be the direction along which you are walking, and the X axis perpendicular to that. Then the coordinates will be displayed on the G-858 in the way most people are used to seeing x and y axes, with the y axis being vertical, and the x horizontal. An example of this set up is shown below.



For this case, the lower left coordinate that you should enter in the Define Map Menu would be (0, 0), and the upper right would be (70, 80). The line spacing is equal to 10, and the mark spacing is equal to 20.

90 Degree Orientation

Suppose, however, that you have already defined the x and y coordinates, and do not wish to define the y axis as parallel to the line direction. One good reason to do this is if you are doing a smaller portion of a larger survey, and you wish the coordinates to be consistent. For example, say you want to survey a smaller area within the last survey:



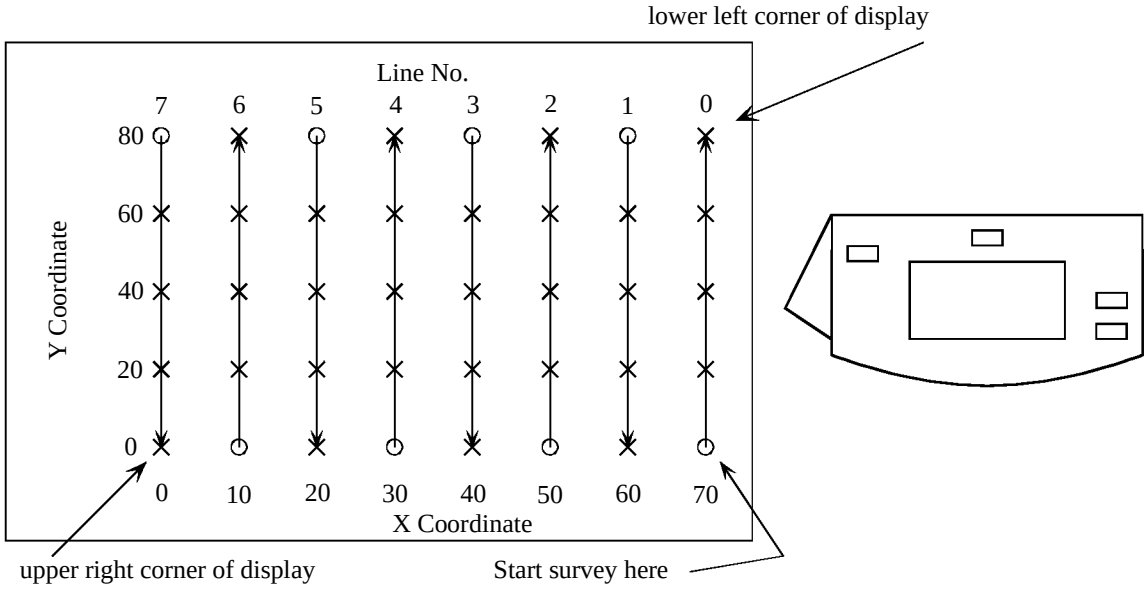
In this case, you would enter the coordinate (10, 60) as the lower left corner of the display, and (50, 20) as the upper right corner of the survey. You would also set the unit to survey parallel to the X axis. You can visualize this by rotating the G-858 clockwise 90 degrees and placing it on the map. For the sub-survey shown, the line spacing is now 20, and the mark spacing 10.

Note: Two things must be remembered in setting up the coordinate systems. First, the line direction is always up and down the G-858 display. Secondly, lines are surveyed starting from the left of the display, and moving toward the right of the display.

180 Degree Orientation

Please note that the G-858 allows you complete freedom in where to start your survey, even though the lines always must move from left to right on the display. You can always rotate the G-858 until the line direction is up and down, and the lines move from left to right. This rotation will determine what coordinate you must enter as the lower left and the upper right of the display. Some orientations will require that you start the survey in the upper left corner of the display. This can be set in the Map Setup Menu before starting the survey.

This can be seen in the following example. Suppose you are back to the original survey, shown in Figure 1, but you wish to start in the lower right corner of the site.



This can be accomplished by rotating the G-858 180 degrees relative to the site map. Then you can see that the correct lower left coordinate is (70, 80), while the upper right coordinate is (0,0). The survey should be begun in the upper left corner of the display.

Advanced Features

The G-858 has many features allowing a great amount of flexibility in defining your position and viewing the survey site. This section describes the ability to define more arbitrary positions, and re-define the survey grid.

Software States

Before discussing the advanced features, it will be helpful to define some states the G-858 can be in, in order to explain when certain operations will work.

There are 3 active states of the G-858 in continuous mode:

Acquire State.

In this state, the system is storing data, generating the woowee tone, and updating the analog sweep trace of the magnetometer output. Pressing the END LINE key sends the system to the Ready State.

Ready State.

This is the state the system is in between lines, for example. Data is not being recorded, the woowee sound is off, and the sweep trace is frozen. Pressing the MARK key sends the system to the acquire state.

Pause State.

The system enters this state from the Acquire State when the pause key is pressed.

Positioning Data

In order to interpolate a position for each individual reading, the system must have a position defined both before and after each segment of readings. Because of this, you cannot press ESC from the acquire state. This would leave a series of readings without an ending position, so the most recent readings could not be properly located.

There are two position recording keys on the G-858: MARK and END LINE. As seen above, these keys, in addition to recording the current position, control the transitions between the Ready and Acquire state. They can therefore be used to start and stop data acquisition.

Press the MARK key at fiducial positions when you want to start or continue data storage. Press the END LINE key at a position when you want to stop data storage. You don't have to be at the actual end of a line to press the END LINE key.

The END LINE and MARK keys also control the automatic tracking of the position. As you have no doubt seen, the positions are automatically updated after each position key press. The MARK key increments (or decrements) the vertical position on the display. The END LINE key advances the horizontal position 1 line spacing.

While using the END LINE and MARK keys to control data acquisition when surveying arbitrarily positioned segments, you must manually update the correct positions.

Manually Entering a Position

You may enter new positions from either the Ready or Pause state. One way to do this is to bring up the map display (press MAP) and move the cursor with the arrow keys. This will allow you to move to any fiducial point. Another way is to bring up the acquire menu (press MENU), and type a new coordinate into the G-858. This allows you to enter positions which are not directly at a fiducial point.

Note: Neither method will allow you to enter points which are not on one of the lines of the survey. To fill in more data between lines, you must redefine the grid. See the section Multi-Grid Surveys in this chapter.

If you are currently in the middle of a series of readings, i.e. you pressed the PAUSE key and haven't yet entered a position, you may only position yourself on the same line you are on.

From the Ready state, you may enter any position along the current line. You can then begin a series of readings from that point.

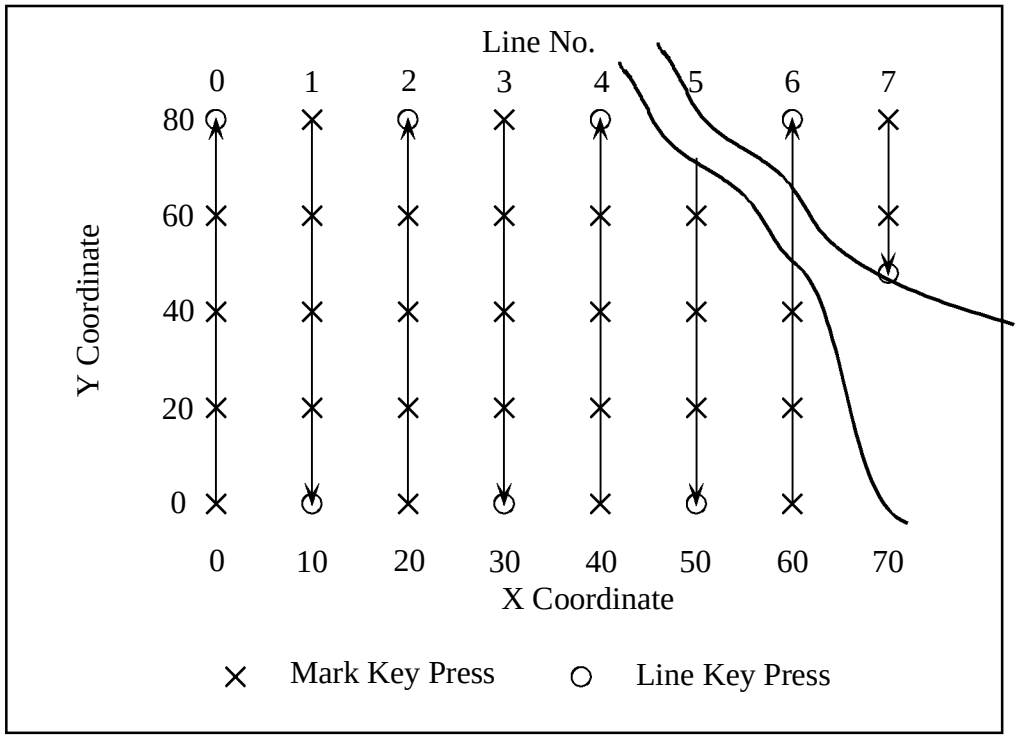
Note: Don't forget to press the ENTER key after entering the value in the numeric entry box.

Example

The principles involved in manually entering positions may best be seen by example. Consider the survey site below, where a stream crosses the survey area. This example shows how to

1. Start a new line at an arbitrary location
2. Leave a gap in the middle of a line.
3. End a line at a specified location

Before going out in the field with your G-858 we strongly suggest that you experiment with this example and observe what happens. This will save much potential confusion out in the field.



Sample Survey Containing an Obstruction.

In the above example, conduct the survey normally until you reach the end of line 4. At that point, press MENU to display the Acqure Menu. Highlight the Next Y field, and enter the value 70. (Press DEL, type 70, then press ENTER). Press ESC to return to the Acquisition Display. Position the sensor at the beginning of line 5 (Y=70), press MARK, and start walking. Proceed normally down line 5, pressing MARK at Y=60, 40, 20, and END LINE at Y=0.

Now begin line 6, by pressing MARK at Y=0, 20, and 40. Upon reaching the stream, press PAUSE. Press MENU, and enter the value 50 into the Next Y field. Press ESC. Press MARK. You have now correctly ended the previous segment of data. After fording the stream, you must enter the starting position of the next segment as described below.

Note: The position entered by an END LINE or MARK key press is the position labeled Next Position on the display. You must update this value *before* pressing the END LINE or MARK keys. If you end a segment by entering an incorrect END LINE or MARK coordinate, the data for that segment will have to be deleted and re-taken, this time with the correct final position.

Press MENU to bring back the Acquire Menu. Enter the position 65 into the Next Y field. Press ESC, then press MARK. You have now entered the starting position.

Note: Entering a value into the Next Y or Next X field in the Acquire Menu will not record the position**.** The MARK key must be pressed to do this, and MARK key presses are only recorded in the Acquisition Display.

To resume collecting data, press PAUSE, and start walking. Press END LINE at the end of line 6.

Note: Notice that data taking was not resumed when the MARK key was pressed. This is because you pressed the PAUSE key when you reached the stream walking up line 6. This puts the G-858 into Pause Mode, and a second PAUSE key press is used to resume data collection. Read the text at the bottom of the Acquisition Display to determine if you are in Pause Mode. If you are, it will say "Press pause to resume." If not, it will say "Press MARK to start" In this latter case, data taking will start when you press MARK. This an important point, so to avoid confusion you should always read the text at the bottom of the display.

Start line 7 normally, by pressing MARK at Y=80 and X=70. When you reach the stream, press PAUSE. Bring up the Acquire Menu (press MENU), and enter 45 into the Next Y field (don't forget to press ENTER). Press ESC,then press END LINE. Notice that you are no longer in the Pause Mode. The END LINE key press moves the system out of that mode.

To observe your handiwork, press the MAP key. You will see that readings are positioned correctly.

Multi-Grid Surveys

As seen above, horizontal locations are limited to grid lines. However, you can change the grid, even in the middle of a survey. This is useful if you want to fill-in parts of a survey with finer spaced lines, or take lines in different directions.

Note: The current grid is used for the automatic tracking of positions, and to define the display extents and fiducial points of the map.

From the Ready state, press ESC to bring up the Mapped Survey Main Menu. Then select DEFINE MAP. Make the changes you desire, then select CONTINUE SURVEY from the Mapped Survey Main Menu. Press the MAP key to bring up the map, and position the cursor where you desire. Then bring back the acquisition display (press ESC from the map). Pressing the MARK key will begin data storage.

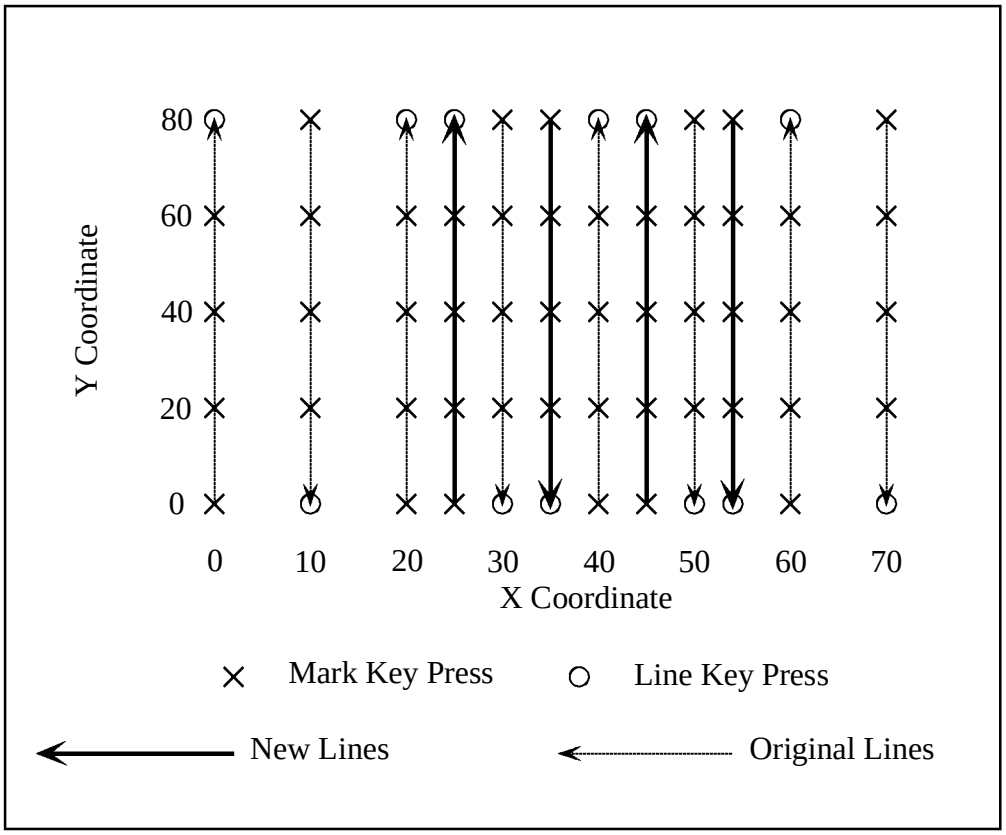
Note: Novices to the G-858 should not attempt this procedure. Another way to do this is to define a new file number, as if this were an unrelated survey. Data can then be located and edited separately, and combined in a program such as Surfer for Windows.

Warning: You may not be able to edit positions in MagMap when using a multi-grid survey. If you use this function, make sure you get the positions correct on the G-858. You must use the NOEDIT method within MagMap in order to locate surveys in which the lines are not parallel.

Note: The map display will only show the current grid. Thus, you may not see data points which were gathered in previous grids. In order to see all of your data points, you could re-define the grid to contain the entire area of interest.

Example 1: Filling in more lines

Suppose you have completed your survey and desire to fill in more lines over a certain portion. Consider the survey shown below.



For the first part of the survey, you would have defined the grid as follows:

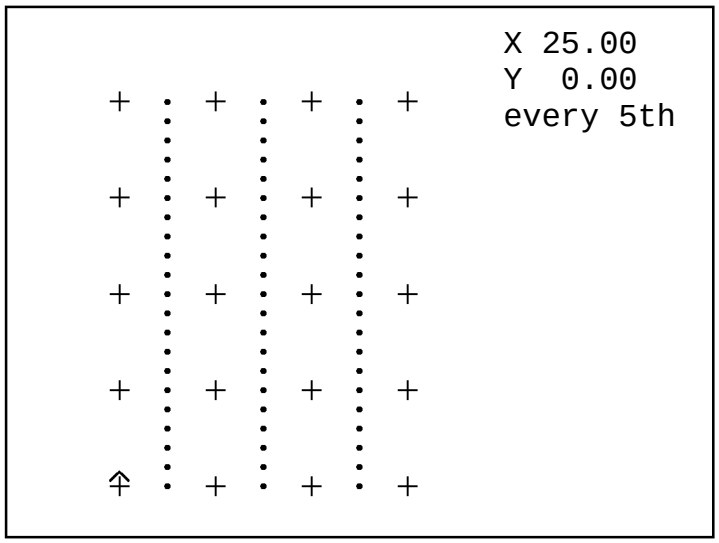
Lower left corner	X= 0.0, Y = 0.0
Upper right corner:	X = 70, Y = 80.0
Survey along	Y axis
Line spacing	10.0
Mark Spacing	20.0

When you have finished the original survey (the light dashed lines), ESC back to the Mapped Survey Main Menu, and select DEFINE MAP. Then enter the following values:

Lower left corner	X= 25.0, Y = 0.0
Upper right corner:	X = 55, Y = 80.0
Survey along	Y axis
Line spacing	10.0
Mark Spacing	20.0

Next, press ESC, then select CONTINUE SURVEY.

Pressing the MAP key will now show what you have done. You should see the following display:



The readings taken for the previous grid are shown. The extent of the map covers only the current grid. However, all data previously taken is still stored in the G-858. You are now ready to survey the new lines in the normal fashion.

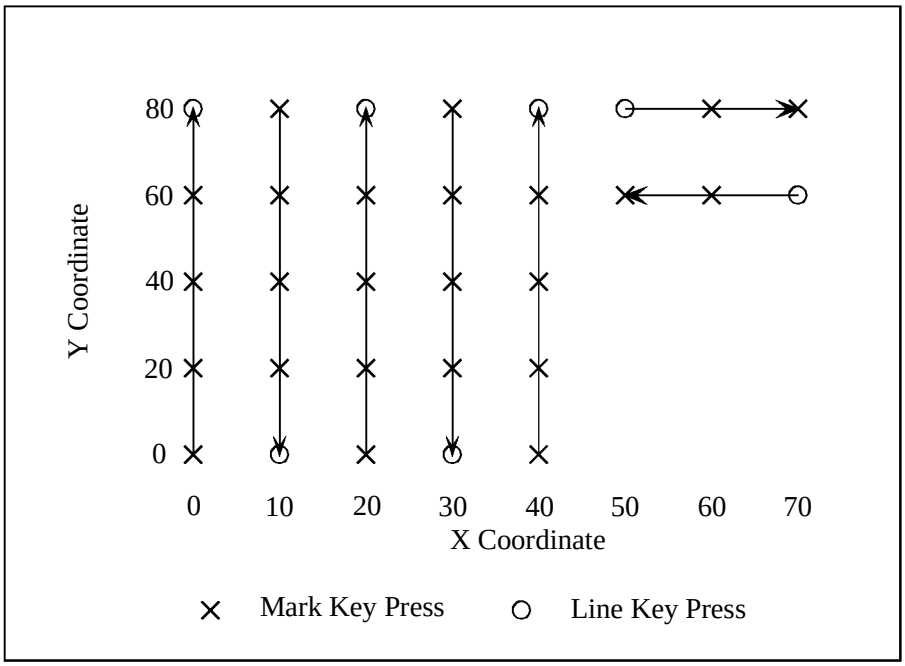
Note: The chart display will not show the old and new lines in the correct order when a multi-grid survey has been performed. The cursor coordinates displayed on the chart display will be correct, however.

Make sure the cursor is positioned where you want it to be. Sometimes, the cursor may not be shown, as it is positioned out of the displayed area. From the map, press MENU, then enter the desired cursor position (X=25, Y=0 in this case). Press ESC to return to the map, and the cursor will be positioned correctly.

After taking all the data of interest, you can confirm that all the data from both grids is still in the G-858. You may do this by re-entering the original grid in the map definition menu, pressing ESC, selecting CONTINUE SURVEY, and pressing MAP.

Example 2

You may also wish to take lines in perpendicular directions. Consider the survey shown below.



For the first part of the survey, define the grid as follows:

Lower left corner	X= 0.0, Y = 0.0
Upper right corner:	X = 40, Y = 80.0
Survey along	Y axis
Line spacing	10.0
Mark Spacing	20.0

When you have finished that, ESC back to the Mapped Survey Main Menu, and select DEFINE MAP. Then enter the following values

Lower left corner	X= 50.0, Y = 80.0
Upper right corner:	X = 70, Y = 0.0
Survey along	X axis
Line spacing	20.0
Mark Spacing	10.0

Then take the next two lines of data. When you download the data, you will be able to locate the points correctly.

Note: MagMap will not be able to edit a survey such as this. You will need to locate the data using the NOEDIT option in MagMap. See Chapter 4 for details.

Chapter 6: Base Station

In base station mode, the unit will not keep track of changes in position. This is most useful when the unit is being used to collect data for diurnal correction of another, roving, unit's data. This procedure is accomplished in the post-processing of your data, using the MagMap program. See Chapter 4 for more details.

In addition, this mode supports a real-time transfer of data out of the RS232. This is useful if you are using another PC to collect and process the data. Of course, you may also store the data inside the G-858, with or without real-time transfer.

Setting up a Base Station Survey

From the main menu, select BASE STATION. The base station main menu will appear:

```
          --- BASE STATION MAIN MENU ---
              File < 1 >  MAG  EMPTY



     Read Mode:       <   TIMED  >
     Store Mode:  < STORE & TRANSFER TO PC >
             Baud rate     <  9600   >
Cycle Time:       [ 0.1      ] s
                 START NEW SURVEY
       10:40:10  02/18/95  Memory Free  86.6%
```

Base Station Main Menu

Scroll to an empty file, or select the base station file you wish to append data to. The fields are as follows:

Read Mode.

May be set to TIMED or TRIGGERED. In TIMED mode, data will be read at timed intervals, set by the cycle time field in this menu. In trigger mode, data will be read and stored by pressing the MARK key.

Store Mode

May be set to STORE IN MEMORY ONLY, STORE AND TRANSFER TO PC, or TRANSFER ONLY. Transferring data means sending it out the serial port as it is being collected. Storing means storing the data in the on-board memory.

Baud rate

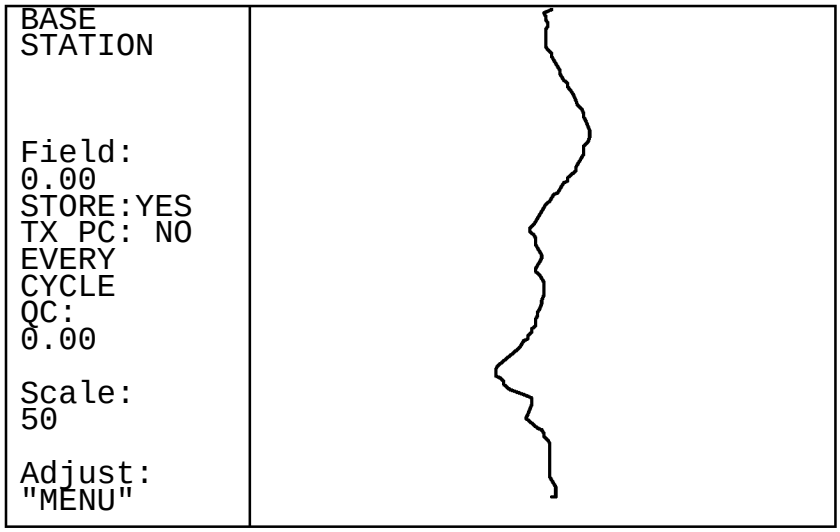
This field is shown only if transferring to PC was selected in the above field.

Cycle Time

Sets the time interval between readings. Also sets the measuring interval. Increasing the measuring interval will increase the sensitivity of the magnetic reading. Setting the cycle time to greater than 1.5 seconds will change the time between readings, but will not affect the sensitivity.

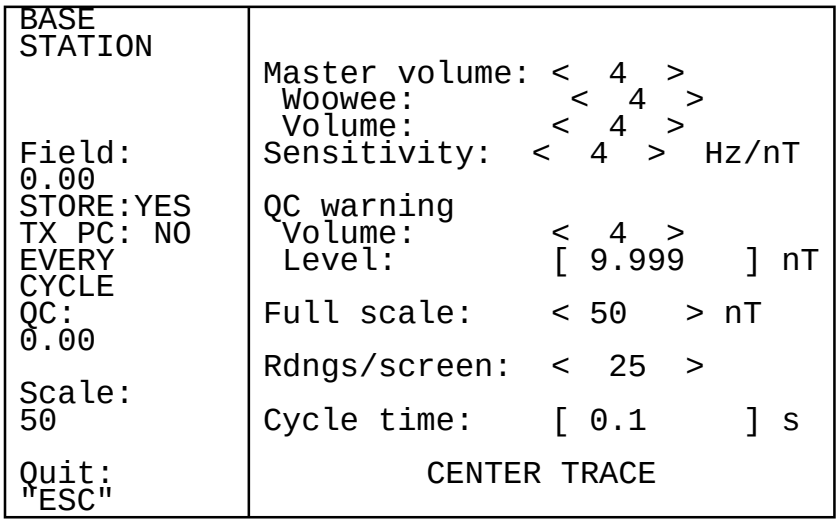
Acquiring Data

Once the parameters have been set to your satisfaction, highlight START NEW SURVEY and press Enter to begin data collection. The base station acquisition menu will be displayed, as shown below.



Base Station Acquisition Display

To adjust certain parameters, press the MENU key to bring up the adjust menu: This will allow you to set the volume, the scale, the woowee pitch and sound level, and center the trace.



Base Station Adjust Menu

The audio and scale may also be adjusted directly from the acquisition menu.

Audio Key

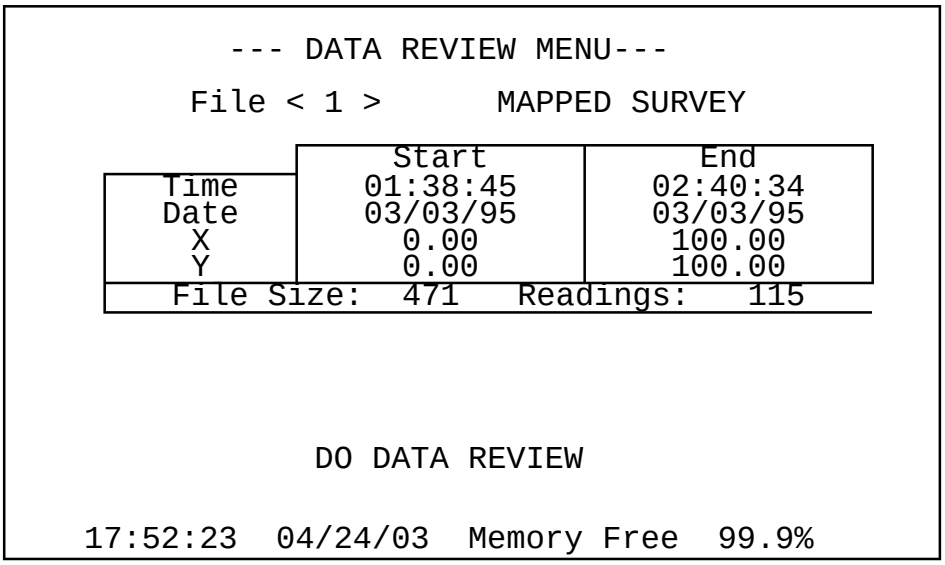
Pressing the audio key will bring up an audio adjust indicator. Then the up and down keys will adjust the volume, while the right and left arrows will adjust the pitch of the woowee. The audio adjust indicator will disappear after a few seconds.

Scale Key

Pressing the scale key will bring up an scale adjust indicator. Then the up and down keys will adjust the speed of the sweep (readings shown per page), while the right and left arrows will adjust the full scale (in nT). The scale adjust indicator will disappear after a few seconds.

Chapter 7: Data Review

Enter the Data Review mode by selecting DATA REVIEW from the main menu. An example display is shown below. Your display will differ, depending upon the type of survey used for a particular file number.



This menu shows the directory of each survey stored in the G-858. Scrolling the file number will scroll through the files.

Selecting DO DATA REVIEW brings up the chart display for the selected file number.

Chart Display

The chart display varies slightly depending upon whether the survey is a simple survey, mapped survey, or base station.

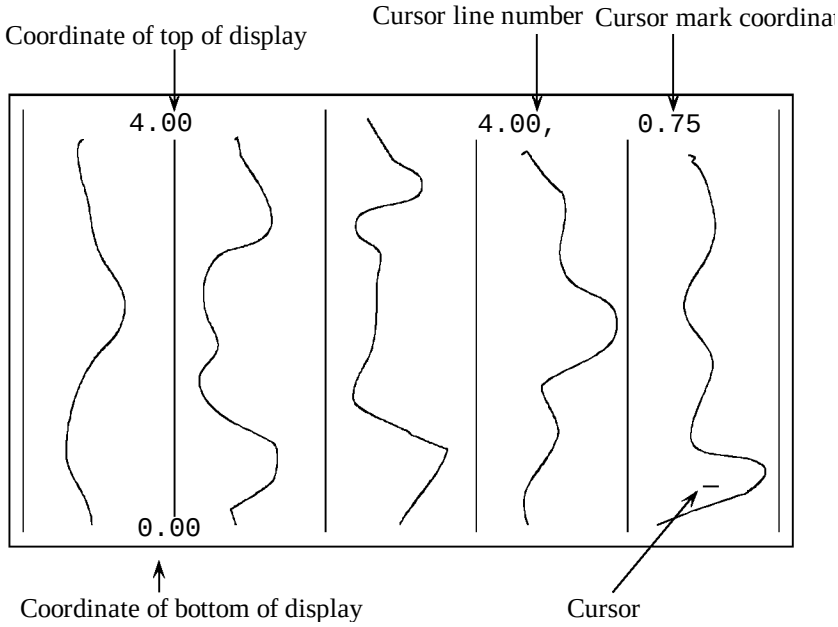


Chart Display for Simple Survey

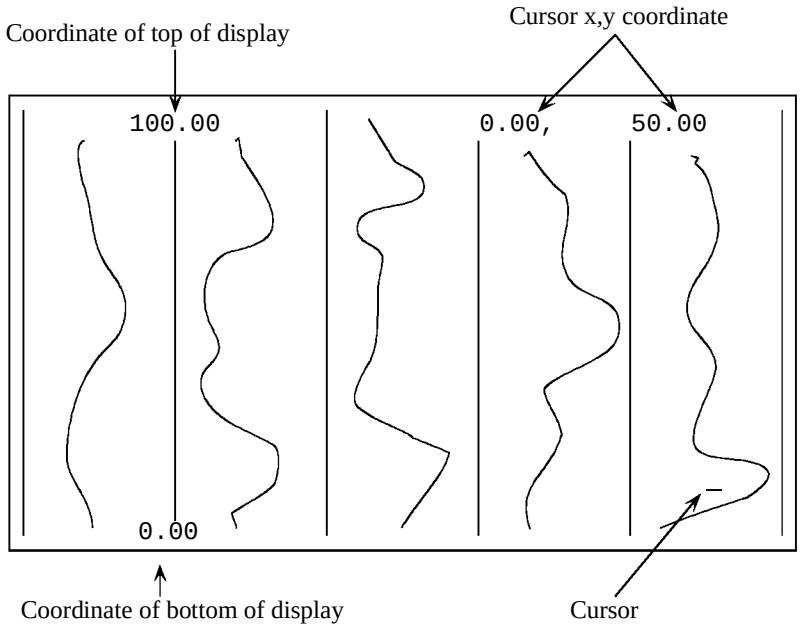


Chart Display for Mapped Survey

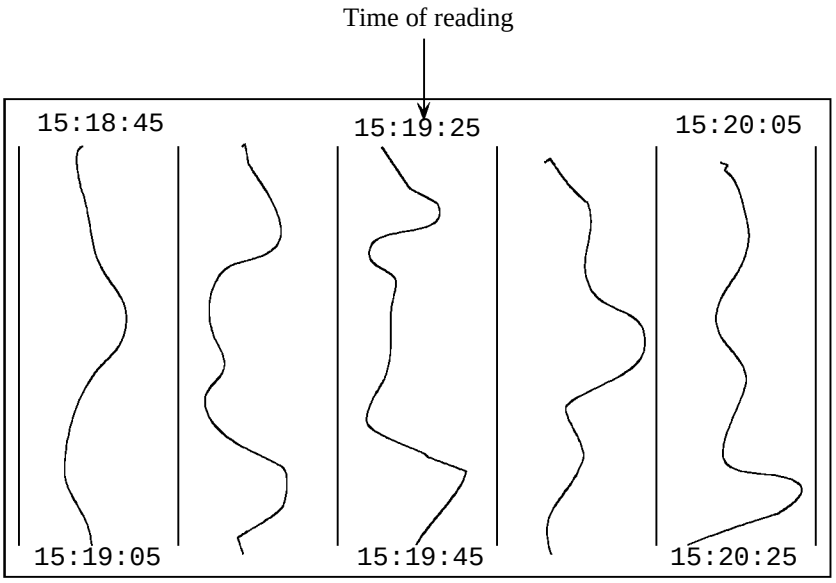
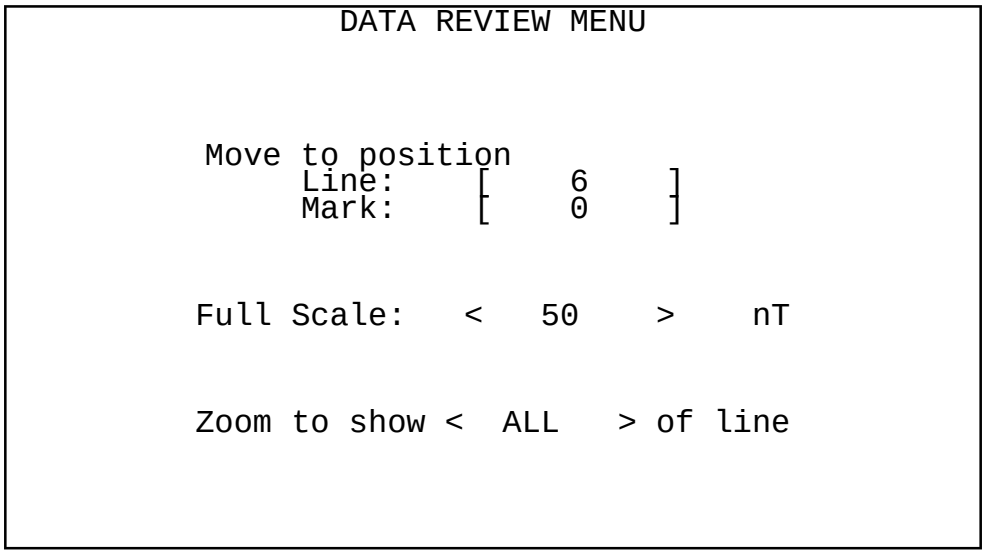


Chart Display for Base Station

The chart display shows profiles of 5 lines of data at a time. The vertical position of the display window is shown on the upper and lower left of the display. The upper right corner shows the x and y position of the cursor.

Data Review Menu

Pressing the MENU key brings up the data review menu



Data Review Menu

The data review menu allow you to go directly to a desired position to view the data without tediously scrolling with the arrow keys. You may also change the horizontal scale, or the vertical scale.

Move to position

You may enter the Line and Mark numbers you which to jump the cursor to in these numeric entry fields. Don't forget to press the Enter key after entering the number.

Full Scale

This shows the horizontal full scale, in nano Teslas of each profile column. The data line will "wrap around" to stay within the window. In other words, if the data line moves off the right side of the column, it will reappear at the left side of the column if the field increases slightly.

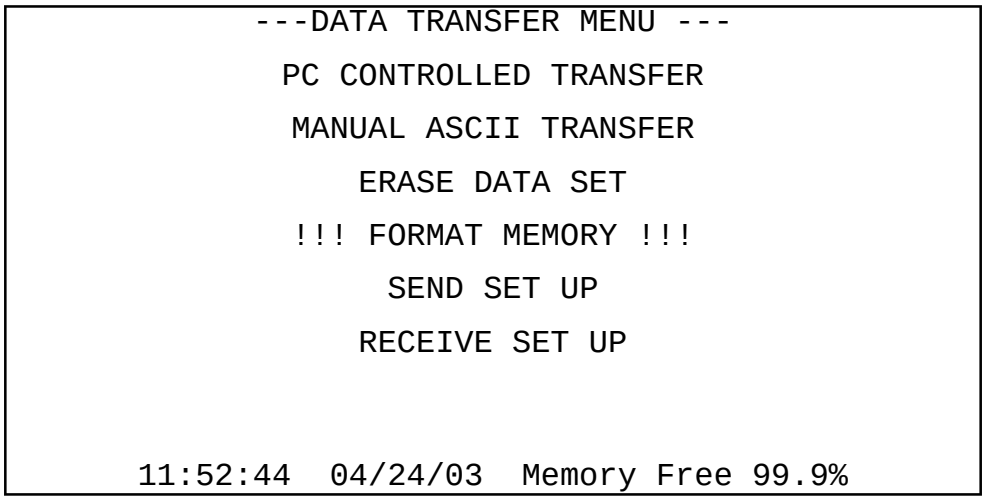
Zoom

This field sets the vertical scale of the display. You may show all of the line, or portions of a line by scrolling through this scroll box with the left and right arrow keys.

If the vertical scale include only a portion of the entire line, you may scroll up the display by moving the cursor with the arrow keys.

Chapter 8: Data Transfer

Selecting DATA TRANSFER from the Main Menu will bring up the data transfer menu:



Data Transfer Menu

This menu allows you to transfer data in either binary form or ASCII form. ASCII data is human readable, but takes about 100 times as long to download. It is suitable only for the smallest files.

Attach the serial cable (supplied with the unit) to the serial port. The other end connects to your PC. Some computers may require a 9 pin to 25 pin serial adapter, available from your computer store. You will need to know which serial port (typically COM1 or COM2) you have attached it to.

PC Controlled Transfer

Allows transfer of data in binary format. Data will be downloaded under the control of the MagMap program on your PC. You must select this option on the G-858 console, then select download from the MagMap program. See Chapter 11, for details on running MagMap. You will also need to know which file number you want to transfer. You may select MANUAL ASCII TRANSFER to page through the files to see which one you want to transfer. Then press ESC to return to this menu, then select PC CONTROLLED TRANSFER.

Manual ASCII Transfer

This allows data to be transferred in ASCII format. See the section below for the sub-menus under this option.

Erase Data Set

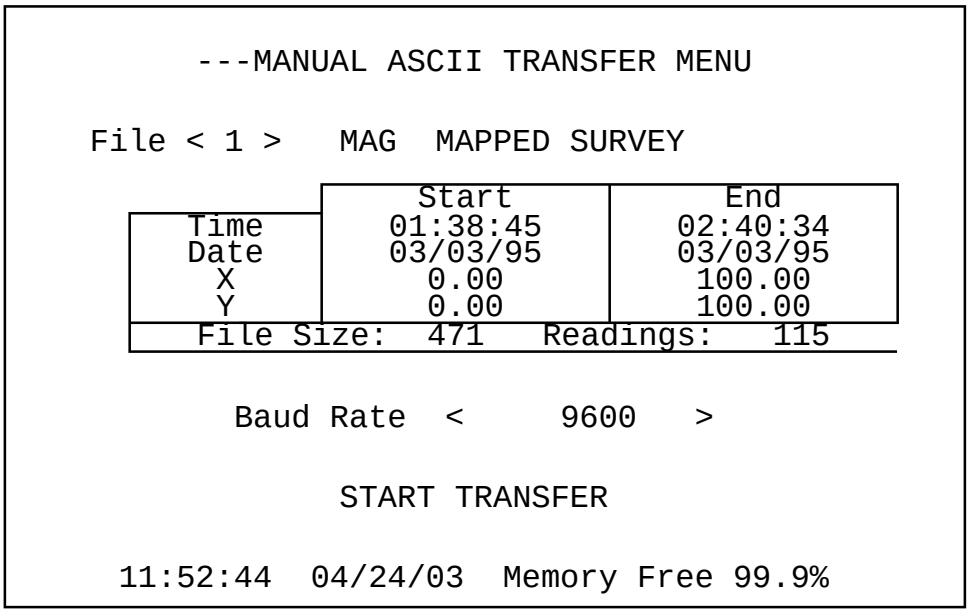
This allows a particular data set (file) to be erased. See the section below for details.

PC Controlled Transfer

Select this option, then run the MagMap software. There, under the Import item of the main menu, you will find options for downloading data. See chapter 11 for more details on running MagMap.

Manual Ascii Transfer

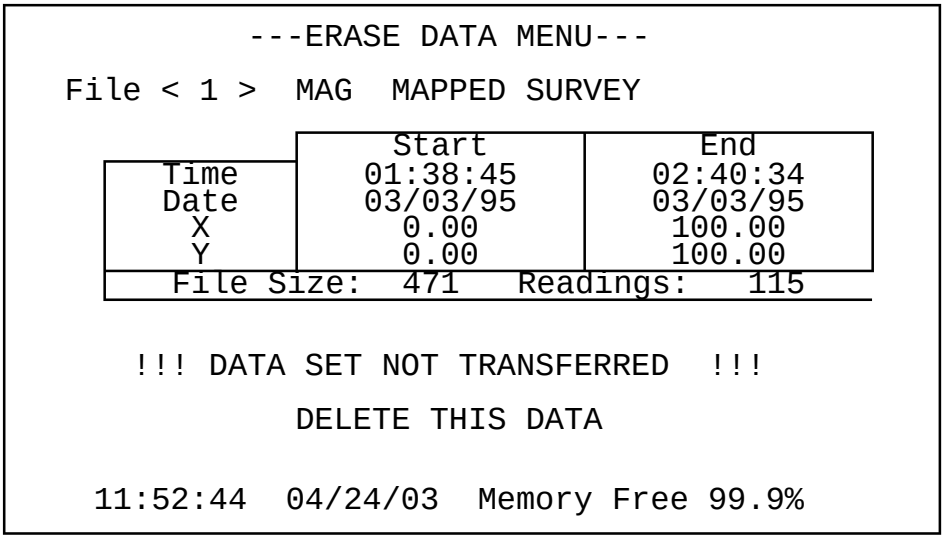
Selecting Manual ASCII TRANSFER will bring up the following menu



You may scroll through the file numbers to the desired data set. Then select the baud rate. Next, you must set up your communications program on your PC. When you highlight START TRANSFER and press Enter, data will be sent out the serial port.

Erasing a Data Set

Selecting ERASE DATA SET will bring up the following menu



Scroll to the desired file number. Then select DELETE THIS DATA. You will be prompted with a dialog box before the file is actually erased. You will not be able to recover any file that you have deleted. Notice the warning message on the menu above for file numbers that have not been transferred. If you have transferred data from this file, this message will not be shown.

Format Memory

Erases the entire data memory of the G-858. All data in all files will be lost. If the system hangs up at some point, you may need to do this after power up to get the unit to behave properly.

Send Set Up

Intended for Geometrics Service and Test.

Receive Set Up

Intended for Geometrics Service and Test.

Chapter 9: GPS

Overview

The G-858 may be used to simultaneously acquire GPS positions while it is acquiring magnetic data. In addition, the G-858 may be programmed to send commands to the GPS receiver when certain keys are pressed. All communication with the GPS takes place through the RS232 port.

The RS232 port of the G-858 is extremely versatile. That feature, and the fact that setting up RS232 communication in general is often confusing, means that you will need to carefully study this section and experiment to get your external equipment to work with the G-858.

Before connecting your GPS to the G-858, please make sure you completely understand how to operate the GPS system. GPS receivers will send data out in many formats, and you must know what commands will tell it to give you the data you wish. You may then program the G-858 to send these commands to the GPS receiver.

Note: Please remember that ASCII strings coming from a GPS unit take up a lot of memory space. Select the smallest data format you can for maximum data collection time. With a GPS unit sending a data string every 1 second in NMEA GGA format, for example, and the G-858 set to collect 10 readings per second, the memory will be full after about 3.5 hours.

Collecting GPS data

First, make sure that the RS232 port is set to collect GPS data. This is done in the main System Setup menu. Set the RS232 port to DATA LOGGER. In addition, you will probably want to set the unit to store GPS data only when in the acquire mode. This means it will store GPS data only when magnetometer data is being stored. Therefore, between lines or within PAUSE mode, no GPS data will be stored. This will save memory, and typically you will not be interested in GPS data during those times.

The next step is to program the commands needed by the GPS unit into the G-858. This is done by selecting EXT RS232 & FIELD NOTE SETUP from the main System Setup menu. See the section earlier in this chapter for information on programming keystrokes to send commands to the GPS.

You will need to connect the GPS to the G-858 using the proper serial cable. Most GPS units will require a null-modem adapter between the supplied RS232 cable for the G-858 and the GPS port. Contact Geometrics for the availability of a cable specially designed for connecting directly to a GPS system.

Once the GPS system is connected, you will need to actually send it the commands you have previously programmed into the G-858. This is most easily done in the CHAT MODE of the EXT RS232 & FIELD NOTE SETUP. Select CHAT MODE, then press the desired keys to send the associated command. You will be able to observe the response of the GPS system from within chat mode. Make sure it is operating properly.

Now you are ready to log GPS data. Start your desired survey as usual. You willl notice a bar indicator which when moving indicates that data is coming in on the RS232 port.

Using GPS data

The GPS data stored during a survey is embedded within the magnetometer and other positioning data. You should upload this data into MagMap2000 where you can filter and plot GPS positions, magnetometer data, destripe (remove heading error), contour and plot the data. Visit www.geometrics.com to download the latest version.

To manually extract the GPS positions from the file, perform the following procedure. First, download the binary file using the MagMap program. If you wish, you can also do any other MagMap function, such as locating the data or doing a diurnal correction. Remember the name of the binary file

(.BIN extension) you used as the output file name when downloading the G-858 data (Import / Download). Exit the MagMap program.

From the DOS prompt run the following program:

`BINTOASC` *`input`*`.bin` *`output`*`.gps -R0 -M0 -D0 -P0 -U0 -F0`

where

`input` is the name of the file containing the binary downloaded data (you must type the .BIN extension

`output` is the filename you wish for the GPS data (you must give it an extension. The `GPS` extension is a suggestion, however, you may use what you wish.)

`-R0 ...` The options tell the program not to extract everything except the RS-232 serial strings. They are a dash, a letter, and the numeral zero.

You will now have created a file of the GPS strings, along with some G-858 formatting information. Lines will be as shown below:

`21` *`DATA_STRING`* `Date Time`

Example (Line is broken only to fit on page. It is actually a single line in the file.)

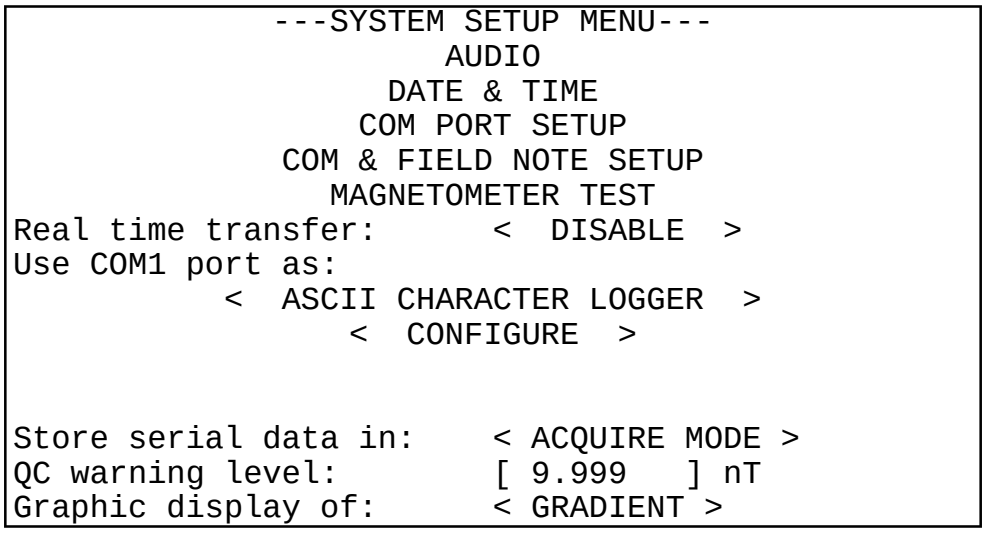
```
21 $GPGGA,175748.00,3726.0363,N,12210.0318,W,0,6,001.1, 00024.6,M,-
028.4,M,031,0000*6C 10:59:14.80 06/01/95
```

The 21 at the beginning of the line indicates this string came in the RS232 port of the G-858. The string is followed by a date and time stamp from the G-858. This may be used to correlate the positions with the magnetometer readings, which are also time stamped.

Note: The BINTOASC program has many other options useful for the advanced user. Type `BINTOASC` at the DOS prompt for a listing of the other options.

Chapter 10: System Setup

Selecting SYSTEM SETUP from the main menu brings up the following menu.



System Setup Menu.

Audio

This allows you to set several parameters relating to the volumes and frequencies of the various audible tones. See below for more details.

Date & Time

Selecting this will allow you to set the date and time. See below for more details.

Com Port Setup

Selecting this will allow you to set the functions and baud rates of COM1 through COM4. This sets the baud rate of the serial for both incoming and outgoing data. Rates are selectable from 1200 to 115200. The system default is 9600. See below for more details.

Com & Field Note Setup

This allows you to define ASCII text strings to be either sent out the serial port or stored as field notes. Sending strings out the serial port is useful for controlling a GPS system. Field notes are useful to mark any desired event.

Each string is associated with a particular key press. During a survey, pressing the key will cause the associated string to be either stored as a field note, or sent out the RS232 port as a command. See below for more details.

Magnetometer Test

This selection opens a screen that provides information about the state of operation of Magnetometer 1 and Magnetometer 2, if connected. Also presented are a selection of internal volatages that indicate the state of the system. See below for more details.

Real Time Transfer

Enabling real time transfer will cause data to be sent out the serial port during the acquisition. The data coming out will be formatted exactly as for the ASCII data transfer. The setting will not affect whether or not data is stored inside the G-858. The options here are 'DISABLE' and 'ENABLE'. When EM-61 data is being acquired this should be set to 'DISABLE'. Sending data in real time to the EM-61 causes the EM-61 to report a huge[*] number of errors.

[*] huge = large enough to cause trouble. The G858 gets bogged down processing these error messages.

Serial Port (Use COM 1 as:)

There are several options for the use of COM 1 as follows:

SIMULATED KEYBOARD
ASCII CHARACTER LOGGER
GEOMETRICS MODULE LOGGER
FRAMED BINARY LOGGER
RAW BINARY LOGGER
EM-61 WITH MAGNETOMETER
EM-61 LOGGER

The "SIMULATED KEYBOARD" mode allows COM1 to appear as an external keyboard, in which case ASCII characters are interpreted as keypad presses. Using your favorite communication package on your PC, you can send key presses to the G-858. The built-in Microsoft Windows accessory Terminal works fine. See the section below **How to Download Commands from the PC.**

The "ASCII CHARACTER LOGGER" mode is used to log RS232 strings are stored in memory as they come in through the COM 1 port. Up to three numbers from COM1 may also be displayed while acquiring data. The display of these numbers may be configured in the "CONFIGURE" line that appears below the " ASCII CHARACTER LOGGER" entry in the scroll list. None to three numbers may be selected and each number may be independently adjusted for bias, scale and 0 to 3 decimal places to display.

The "GEOMETRICS MODULE LOGGER" mode is used to log data from all products that comply with the "GEOMETRICS MODULE" format. These include the CM201, the CM221, the G880, the G881 and the OhmMapper. Readings from these can be used in place of the G858's sensors. The display of these numbers may be configured in the "CONFIGURE" line that appears below the "GEOMETRICS MODULE LOGGER " entry in the scroll list. Up to two numbers with decimal points may be detected and logged as magnetometer field values. Zero to three numbers may be selected and each number may be independently adjusted for bias, scale and 0 to 3 decimal places to display.

The "FRAMED BINARY LOGGER" mode is currently only used with the MineLabs EM system. The readings from this are used in place of the G858's sensors.

The "RAW BINARY LOGGER" mode would only be needed if what is being received is binary data of a format other than "FRAMED BINARY". Each received byte is simply converted into two hexidecimal digits "0..F" and stored.

The "EM-61 WITH MAGNETOMETER" mode allows an EM-61 to be connected and logged as ASCII while a magnetometer sensor is also connected. The odds of an EM-61 not interfering with the magnetics measurement are very near zero, but if it can be done, the G858 is ready for it. The EM-61's battery voltage will be displayed as described below. The logging of the EM-61 may be configured in the "CONFIGURE" line that appears below the "EM-61 WITH MAGNETOMETER" entry in the scroll list.

When cycling is set to "G858 timing", the EM-61 will be commanded to cycle by the G858. The command will be sent at the rate specified by the G858's cycle time setting.

The EM61 system has a built in encoder on one of its wheels. If you wish to use this you should select the "wheel encoder" option here. The cycle time setting of the G-858 will only serve as a time out time for receiving data from the EM-61. The EM-61 will send its data based on the rotation of the wheel.

The "manual button" mode is very like the "wheel encoder" mode. In this case the manual button on the EM-61 will cause a measurement.

After processing the EM-61's data to make a reading, you have three options of what to do with the string from the EM-61.

The "THROW AWAY THE REST" option means just that. The battery voltage and the "fine time" from the serial data will be discarded.

The "STORE THE REST AS SERIAL DATA" option causes a serial string consisting of only the battery voltage to be stored along with the "fine time" information.

The "STORE ENTIRE STRING AS SERIAL" option causes everything that came from the EM-61 to be stored as serial data as well as being stored in place of magnetics readings.

The "EM-61 LOGGER" mode allows the readings from the EM-61 system to be used in place of the magnetometer readings. Whenever the G858 is placed in any of the acquire modes (Search, Simple survey, Mapped survey) the battery voltage from the EM-61 will be displayed as a three digit number in the upper left part of the screen. . The logging of the EM-61 may be configured in the "CONFIGURE" line that appears below the " EM-61 LOGGER " entry in the scroll list. See the "CONFIGURE" line explanation just above.

Storing Serial Data (Store serial data:)

The storing of input ASCII text may be set to occur only when magnetic data is being recorded, "WHEN ACQUIRE" is selected (see the description of Acquire mode), or whenever the display is in the active state, "ALWAYS" selection (Acquire, Ready, or Pause modes). For a GPS system, you will typically be interested in collecting data during the Acquisition mode only.

Warning: Data will never be stored if the unit is displaying a menu, the map, or the data review profiles.

QC Warning Level:

This sets the level above which the QC will causes a warning tone to be sounded.

Graphic Display

This field is shown only if the Gradiometer option has been installed, and two sensors are attached to the unit. See the section on Gradiometer for more details. The selections are "FIELD1", "FIELD 2" or "GRADIENT".

Audio Setup

There are several audible indicators on the G-858. Selecting AUDIO will bring up the following menu.

```
                AUDIO SETUP MENU

      Master Volume                 <  4  >
      Metronome Volume              <  4  >
      Metronome cadence (Beeps/min) [  60 ]
      Woowee volume                 <  4  >
      Woowee sensitivity            <  4  >
      Warning volume                <  4  >
      QC warning volume             <  4  >
      Mark/line key event volume    <  4  >
```

Master Volume

This field adjusts the level of all the sounds. 0 is the quietest, 9 the loudest.

Metronome Volume

This adjust the volume of the metronome. This metronome may be set to help you maintain a steady pace when surveying a site. 0 is the quietest, 9 the loudest.

Metronome cadence

This adjust the frequency of the metronome pace.

Woowee volume

The "woowee' is the audible indicator of field strength. It is particularly helpful when searching for anomalies in Search Mode. This sound is active only in continuous survey mode.

Woowee sensitivity

The frequency of the woowee noise changes with changing field strength. This number represents the amount of frequency change per increment in field strength. If the field is fairly smoothly varying, set this to a higher number. For fields with large variations, set to a smaller number.

Warning volume

This sets the volume for warning tones.

QC warning volume

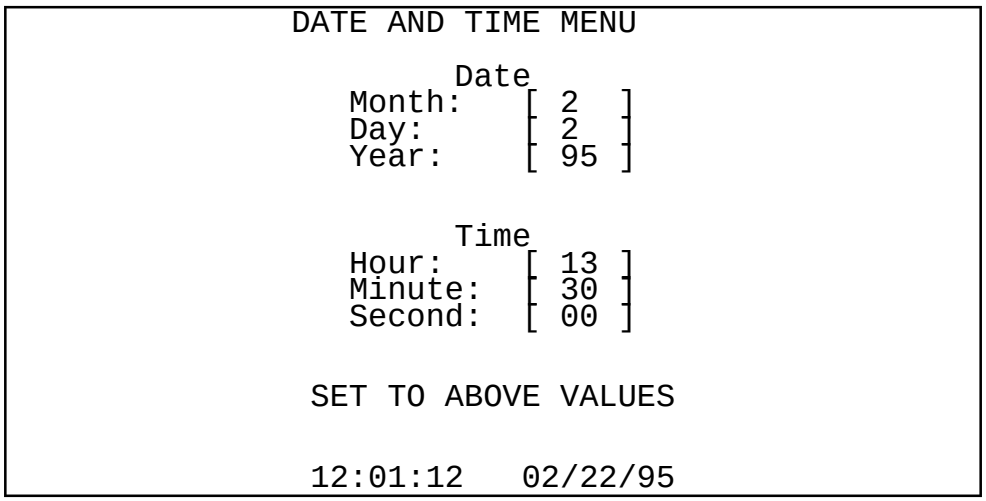
This sets the volume of the QC warning tone.

Mark/line key event volume

This sets the volume of the key click noise when you press a position key

Setting the Date and Time

Selecting DATE & TIME form the System Setup Menu will bring up the following display.



Date and Time Menu.

Enter the correct values in the numeric entry fields. Don't forget to press Enter after entering the value. Then highlight SET TO ABOVE VALUES and press Enter.

COM Port Setup Menu

Selecting COM PORT SETUP from the System Setup Menu will display the following menu:

```
         ---COM PORT SETUP MENU---
COM1 and COM4 PORT MODE: < 1 >
   COM1 is RS232 I/O
   COM4 is RS232 input
COM2 and COM3 PORT MODE: < 1 >
   COM2 is RS232 I/O
   COM3 is RS232 I/O
COM1 baud rate:     < 9600 >
COM2 baud rate:     < 9600 >
COM3 baud rate:     < 9600 >
COM4 baud rate:     < 9600 >
```

COM1 and COM4 Port Mode:

Mode 1 is COM1 is RS232 I/O and COM4 is RS232 input.
Mode 2 is COM1 is RS232 I/O and COM4 is pulsed input.
Mode 3 is COM1 is RS422 input and COM4 disabled.

COM2 and COM3 Port Mode:

Mode 1 is COM2 is RS232 I/O and COM3 is RS232 I/O.
Mode 2 is COM2 is RS422 input and COM3 is disabled.

COM(x) baud rate:

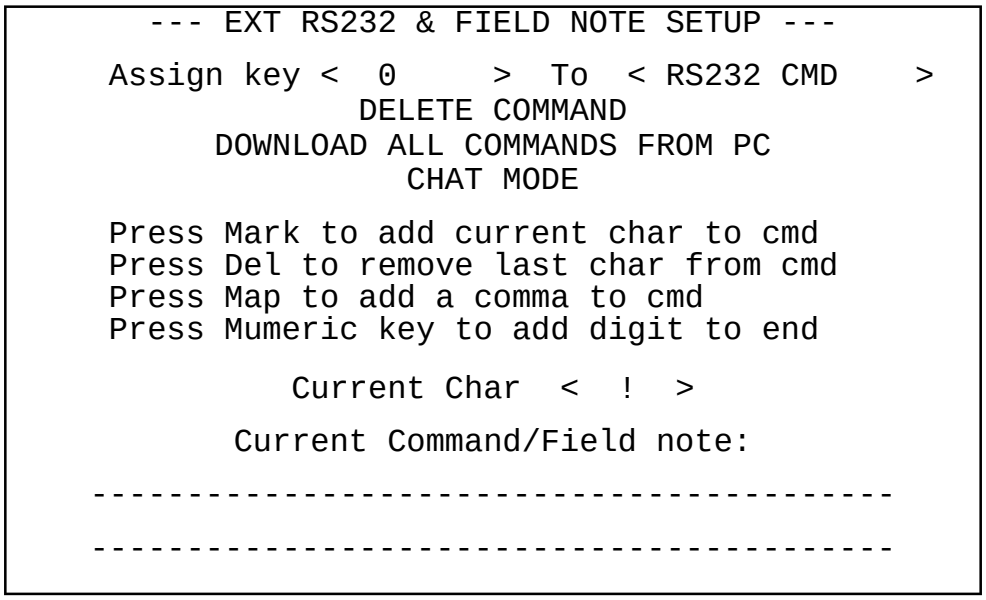
The selections available for baud rates are:

1200
2400
4800
9600
19200
15200

The factory default is 9600.

External RS232 and Field Note Setup

Selecting this item will bring up the following menu:



Assign Key Field

This scroll list sets which key press is associated with the ASCII string.

Function Field

This scroll list sets up the key as either a RS232 Command or a Field Note. RS232 commands are sent out the serial port, while field notes are stored in the internal memory.

Delete Command

Pressing ENTER on this field will delete the entire command from memory.

Download all commands from PC

You may download an ASCII file from your PC to set up the entire set of commands. This is strongly recommended, since entering them from the scroll list below is very tedious. See the section below on how to set up and transfer a file of commands from your PC.

Chat Mode

This will enable you to observe the ASCII text coming from whatever device is connected to the serial port.

Current Character

You may scroll through this list to the desired character to add to the present command. Pressing the MARK key will add it to the end of the command. As a handy shortcut, you may press any numeric key to add a numeric character. There is no way to insert characters in the middle of the command. This manner of entering a command is so tedious, we recommend using it only if you forgot to download a needed command when you were near a PC.

How to Download Commands from the PC

Use your favorite ASCII text editor (DOS Edit or Windows Notepad are easy and readily available) to create a file as shown below:

```
G858CMD,00,$PASHS,NME,SAT,A,ON
G858CMD,01,$PASHS,SPD,B,2
G858CMD,02,$PASHS,RTC,REM,B
G858CMD,03,$PASHS,RTC,BAS,A
G858CMD,04,$PASHS,RTC,TYP,9,1
G858CMD,05,$PASHS,NME,GGA,A,ON
G858TXT,06,Fell into a hole
G858TXT,07,Dropped the magnetometer
G858END
```

The first six lines set up RS232 commands. The keyword G-858CMD determines this. The second field, the two digit number, specifies which key the command or note is associated with. The numbers 00 through 09 correspond to the number keys on the console. The other keys are as shown below:

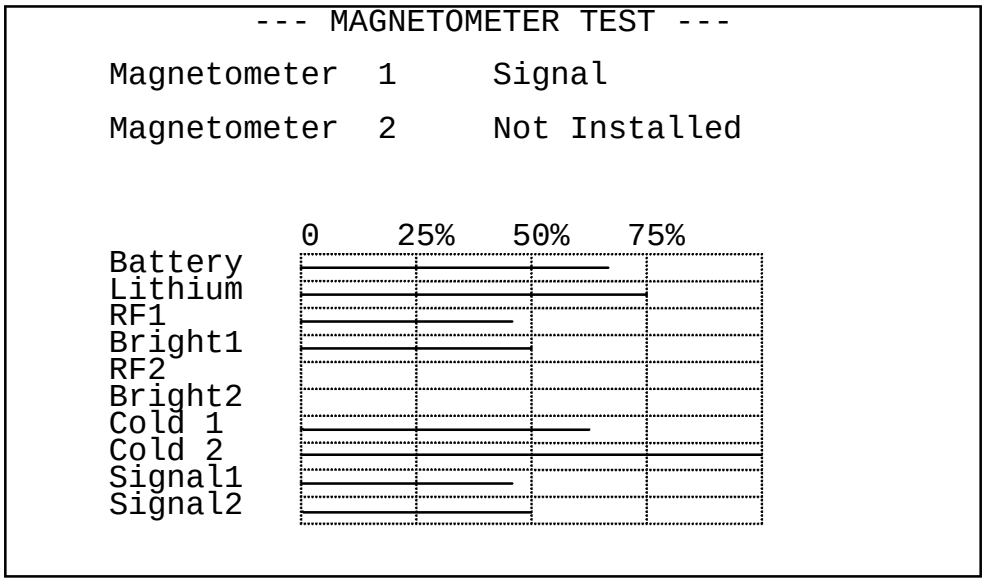
10	MARK	15	CHART
11	LINE	16	MAP
12	PAUSE	17	ENTER
13	ESC	18	POWER
14	MENU		

Note: The ASCII commands or field notes will only be active during the one of the active modes of operation. These are the Ready state, Acquire state, and Pause state, as explained on page 53.

Each key also retains its normal function. For example, if the MARK key is assigned to an RS232 command, pressing it will still perform the normal MARK key function. This is useful, for example, if you wanted to store a GPS reading only at each MARK location. Then, you would program the MARK key with the command to query the GPS for the current position. In doing this, you would probably also want to program the END LINE key with the same command. Then, you will get a GPS confirmation at each fiducial point.

Magnetometer Test

The magnetometer test brings up the following display:



Magnetometer Test Display.

The first two lines, showing the status of the sensors, are very useful to watch if no signal is seen, and during system warm-up.. The possible states of the sensor are as follows:

Not installed. Indicates the sensor is unplugged.

Initializing. Checking for presence of sensor.

Warming Up. Sensor is being warmed up to the operating point. This may take several minutes in cold temperatures.

Starting Lamp. Energy is being applied to the sensor lamp to try to strike it. Should occur only briefly after sensor is warmed up.

Running up. Cesium cell is being warmed up to the desired temperature.

Regulating. Cell is operating, apparently normally, but a valid signal is not present. Usually occurs due to high field gradients, or the field being in a dead zone.

Signal. Sensor is reading a valid signal.

Failed. There was some problem in either striking the lamp or maintaining the desired brightness or temperature. Usually, unplugging the sensor and plugging it back in will eliminate the problem.

Next, the graph shows various internal voltages. A description of each item follows:

Battery: Indicates the voltage of the main battery. Full power is shown as 60%.

Lithium. Indicates the voltage of the internal lithium battery, which is responsible for storing data and setting when the unit is turned off. Normal operating range is 65% to 75%.

RF 1 and RF 2 Indicates the drive level being applied to the cesium sensor lamps. Normal operating range is 25% to 75%.

Bright 1 and Bright 2 Indicates the resulting lamp brightness. Should be maintained at 50%. During warm up, this voltage will slowly settle at that value.

Cold 1 and Cold 2 Indicates the cesium cell temperature. Should be maintained near 50%. Larger numbers mean cooler cells.

Signal 1 and Signal 2. Indicates the signal strength. Signal strength is a funciton of cell orientation and field value. Normal strengths are between 5% and 25%.

Chapter 11: MagMap2000 Software

The MagMap2000 software program provides the G-858 user with data downloading and editing capability. Acquired data is downloaded via high speed RS-232 communications link and then manipulated to generate or edit interpolated X-Y or GPS position information. Editing functions include shifting lines, changing the direction of lines, appending or cutting lines, and deleting or inserting segments of lines or entire lines. Vertical and horizontal (longitudinal and transverse) gradiometer data processing is supported. The program offers destriping and other filtering routines for data cleanup. The resulting data grid is graphically displayed on the PC as a quality control measure and to assure coherence between the original acquisition parameters and the final locations. In addition the program provides simple gridding, contouring and plotting (printing) of the positions, track plots and magnetic contour maps. In addition the data can be exported in formats compatible with Surfer for Windows (*.DAT) or Geosoft OASIS (*.XYZ).

Because of the power and complexity of the MagMap2000 program, its operation will not be covered here. Please refer to the MagMap2000 Manual for complete instructions on the use of the program. Also note that the MagMap2000 Manual, the MagMap2000 program and this manual are available on our web site www.geometrics.com under Downloads, FTP, PUB, MAG. We recommend that you regularly visit our site for the latest software upgrades.

Appendix 1: Surveying Principles

This section outlines the principles of performing a magnetic survey. It covers setting up and performing the survey and locating items of interest within anomalies.

Guidelines for Small Ground Magnetometer Surveys

The general comments below cover only the site layout and preparations for a survey. The survey objectives, determination of parameters for the instrument data collection and the actual data processing and map preparation are covered elsewhere.

In order to accomplish a successful ground survey, each of the elements of magnetometer data acquisition, path over the ground from which the data are recorded, and processing of the data into map form, must be handled in a precise and accurate manner. Each element is completely interdependent upon the others and if one is compromised in quality or accuracy then all are compromised. During a survey, possibilities for error are numerous and great care and concentration are required to avoid mistakes, some of which may be so serious as to require starting the survey over. The focus should be toward completing the survey completely error-free.

Typically, the most difficult surveys are those involving detection of small magnetic targets and the presentation of an accurate 1 or 2 nT contour map. In these cases, the survey must include: a close line spacing (1-2 m) with precise tracking in both the X- and Y- directions; diurnal correction (0.5 nT or better); correction of heading errors from instrument and/or operator; maintaining the sensor a constant distance above the ground; and absolutely no mistakes in procedure and data processing.

Number of People

Under certain conditions, the survey can be laid out and run by one individual; but this is rare and risky. It is far better to have a minimum of two people closely involved and ideally, three or even four people. Not only must the layout and marking of the survey lines be considered but also an individual must be designated to maintain a separate survey log, set up the base station, and operate the portable magnetometer. Note also that the operator doing all of the walking may require relief, for oftentimes the terrain and distance conspire to make his job very grueling.

Survey Efficiency

Speed and cost-efficiency in completing the survey is of course the ideal objective. This does not, however, require the use of innovative short cuts, new gadgetry or excessive manpower, but rather the avoidance of mistakes and errors. To prevent wondering off line even once in the course of a survey, with all of the attendant time spent sorting out and making the corrections, easily justifies a slower but more positive method. Efficiency will only be achieved by avoiding confusion, the correction of errors, and by the use of fail-safe procedures. All of the methods suggested below are simple low tech, and relatively slow, but proven effective. They can easily be improved upon but only at the risk of greater time, survey quality, or greater cost. So in the beginning, keep it as simple as possible.

Layout of the Survey Track

Having determined the optimum line spacing, layout the survey area in a square or rectangular format with the lines running N to S if possible. Use a Theodilite if available, otherwise use a measurement tape (non-stretch) of the required length. Designate one side of the area to be the "baseline" and layout and mark on this line each survey profile. Note that any stakes driven into the ground must be non-magnetic. (Wooden stakes driven into the ground will work well but may not be visible at distance.) If the site will be reoccupied in the future, it may be desirable to drive a one-meter iron rod (re-bar) into the ground at each corner of the survey area as a permanent marker. Since the profile line markers may not be visible at a distance, a method must be found that will allow the Magnetometer operator to locate and follow the line: a light cord or rope stretched on the ground between the beginning and end of each line; a long PVC pipe or other colored marker to be held at the end of each line and then sequentially moved; use of spray paint to mark a series of dashes along the path of each line, etc.

If the terrain is rough or bushy, ground markers along each line will be essential. Otherwise, if the terrain is flat and each end of the line is readily visible, a marker at each end and in the center may suffice. (The operator should have at least two markers to line up on when starting a line.) Whatever method is chosen, it must be completely non-magnetic, positive, easily moved in a coordinated way, and must give the operator a precise direction.

Note that coordination between the people moving the markers is sometimes difficult and frequently a source of error. In addition, if the survey lines are closely spaced, e.g., one- or two-meter separation, the Magnetometer operator may have trouble distinguishing between which marker to head for. The most certain and positive method in all cases is to mark the path by stretching a light string or rope the entire length of the pathway; or, to paint or otherwise mark the ground at short intervals.

If the area to be surveyed is larger than say 100 x 100 meters or difficult to walk through, then the area should be broken up into convenient sub-sections which overlap by at least one profile line. If some sections of line are not passable, then provision should be made for the operator to detour around them but only after establishing a procedure to stop/start (pause) and annotate the data. (This must be foolproof, simple and fully coordinated with the data processing.) Note that the Magnetometer operator must be aware of what line he is on at all times and the line number must agree with the line number recorded in the data. This is once again a frequent source of error and should be double-checked by another person.

In no case should a survey be started until all lines have been laid out and marked, and all aspects of the survey carefully re-checked. A few hours more or less at this stage means very little. What is crucial is to prevent major errors (or even minor ones) that may cost extra days of time and effort.

Diurnal Correction

There are many types of surveys that do not require correction for time varying field errors (diurnal). Generally they involve large magnetic targets such as pipelines and tanks, or coarse line spacing, or where the survey may be accomplished in a very short period of time. In these cases, once it is determined that a severe magnetic storm is not in progress, the survey can proceed without the normal base station correction and with good reliable results.

Note that the high measurement rate of the G-858 allows a rapid walking speed along the profile line. Thus, even large target anomalies are covered within tens of seconds, reducing the potential Diurnal effects.

Surveys that involve very close line spacing, small or subtle targets or where the maximum accuracy is desired require diurnal correction from a base station installed close to the survey area. Ideally, equal sensitivity and measurement rates to the field instrument should be employed in the base station. In general practice, whatever instrument is available is used. In most cases this works well even during periods of relative high field activity.

It should be remembered that "diurnal error" will have the same effects in the mapping process as "location error", and that without correction, low amplitude/high frequency anomalies could appear in the measured data that would seem to be targets but would in fact not be real. In addition, if the survey has been broken up into blocks that are acquired on different days, the blocks will not fit smoothly together unless a diurnal correction is made and their D C level shifted.

There are also other types of local magnetic field disturbances that can seriously effect the map accuracy and quality. These include ground currents and other local AC or DC fields from power lines or urban electric trains or trolleys. Of these, electric trains or trolleys are the more serious as their effects may be large in amplitude and extend for many miles. Usually it is more effective to complete the survey at night when these noise fields are greatly diminished.

Survey Accuracy

Commercial survey specifications may allow an “off line” error of up to ±20% (or more) of the line separation. For a magnetic object having an anomaly extending over several lines, this amount of location error does not prevent the object’s detection but does distort the anomaly’s shape, its peak-to-peak amplitude and its true location. Large changes in speed along the profile line will have a similar effect but can be prevented by the use of intermediate waypoints. (The worst case condition would be “off line” by +20% in one direction and "off line” by -20% in the opposite direction with each line having a 10% change in speed.) Location errors of this magnitude will not seriously change the overall correctness of the final map, considering that this type of survey is primarily for detection/location. This is not the case, however, if the location errors substantially exceed ±20%, e.g., off by one or more line separations. This amount of error may cause targets of interest to go undetected, or target anomalies to be shifted in location, resulting in, at worst, an erroneous map or at best an untrustworthy one. Careful layout and accurate tracking along the line will avoid these problems.

Survey Credibility

How does a client or survey manager know that a survey has been conducted properly and that the results are correct and believable? He examines the finished contour map for gross errors in data fit, location of target signatures, and overall map quality.

1) Selected anomalies that have been detected are re-acquired to see if they are in the proper location.
2) The raw data are examined to insure that line numbers are correct, data corrections have been properly executed, etc.
3) Selected tests are made on the finished data, e.g., a plot of “stacked profiles” to determine that start/stop points are correct, speed changes are not excessive, there are no data gaps, etc.

Location of Small Objects Within Associated Anomalies

When data has been acquired over an area and processed into map form, it is often necessary to reacquire the location of each anomaly and dig to expose the ferrous object. The relocation of the anomaly is relatively simple since the coordinates can be taken directly from the map produced. However, the exact location of the object within the anomaly is often times difficult to identify and the convoluted magnetic field can be very confusing.

The anomaly may be sharp and steep (high frequency) indicating a small object close to the surface. It may be just one peak or it may be multiple peaks depending upon the object's shape, its orientation within the earth's field, and whether the anomaly is largely due to permanent or induced effect. It may appear as a dipole or monopole, and its shape on the map may be further distorted by the distance between profiles, especially if this is large with respect to the object size. Each of these factors will also affect the anomaly signature when the object is much larger in ferrous mass and/or is buried much deeper with the resultant areal coverage of the anomaly much larger (low frequency).

As one sweeps the G-858 sensor over these peaks, it is difficult to conceptually grasp their significance, especially when using the audio output as a reference. To reduce confusion and to provide the basis for a systematic approach, it is very helpful to produce a 3-D map showing each of the peaks and valleys with the perspective of depth. Generally, a high and low pair (monopole) will stand out from the rest of the peaks and if these peaks are relocated using the G-858, the object will be midway between them.

When undertaking this exercise in the field, the audio tone should be turned down or even disregarded with the visual display of the earth's field on the front panel becoming the primary focus. By slowly moving the sensor over the anomalous area, the exact high and low peak can be located and a spot on the ground marked for each. A dipole, in the earth's field inclinations of greater than 60° will have its low North of the high peak, and in horizontal fields (inclination of 0°), the low will be in the center with a high at the North and the South ends. The point midway between high and low will contain the highest gradient and will be directly over the object or very close to it. In those cases where there is only one strong peak, the object will be directly beneath the peak.

For very large anomalies the distance between high and low peaks may be two to ten meters or even greater. To reduce the amount of digging, it is suggested that a short profile be run completely over the anomaly, passing directly over each peak previously located and marked on the ground. Viewing this profile on the G-858 display will allow the estimation of the point of inflection of the curve between the peaks indicating the point of maximum Gradient (which should be directly over the object), and the depth of burial by means of the half width rule. (Refer to chapter V of Applications Manual for PortableMagnetometers.)

Appendix 2: CSAZ

Cesium Sensor Azimuth Program

CSAZ is a program written by Geometrics for users of Cesium magnetometers. The purpose of the program is to determine the proper orientation of the Cesium sensor at various earth's field dip angles. AZ stands for azimuth.

The program is located on the MagMap install disk included with the G-858. Once MagMap is installed, CSAZ will also be installed.

The program is easy to operate. Begin by typing CSAZ. You will see a towed bird with the sensor mounted vertically. A lower graphic image displays the bird from a vertical perspective. If you are using the program for land or marine applications, the orientation of the bird can be taken to be the orientation of the sensor staff or fish.

The first piece of information required is the earth's dip angle in your survey area. Refer to Geometrics' Application Manual for Portable Magnetometers, page 5, and select the angle from the map. For instance, the dip angle in San Francisco is 62 degree, Chicago is 72 degrees, Sao Paolo is 30 degrees and Singapore is 18 degrees. Next enter a N or S for the hemisphere (no enter key required here).

First we recommend that you just press enter twice for no tilt and no rotation, as shown in Figure 1. After a few moments you will hear a beep when the computations are completed. Press any key to see the graphical display of the signal to noise ratio of the sensor in that orientation at that dip angle. This is shown in Figure 2.

The circumference of the graphic represents the compass directions in degrees, i.e. the survey direction. The white portion of the graphic emanating from the center is the proportional signal-to-noise ratio. The center ±15 degree cone is the dead zone, so the informational part of the display is represented by that part of the "white" area that
is outside of the 15 degree circle. The longer the white line, the better the response of the magnetometer in that direction.

If the white line terminates inside the 15 degree circle, then you will get no signal traveling in that direction. If it terminates just outside the 15 degree circle, then the installation will tolerate very little in the way of yaw, pitch or roll (depending on orientation, but most likely yaw) of the sensor before the earth's field vector goes into the sensor dead zone. Longer lines are better.

Next, press escape and re-enter the dip angle and hemisphere information. Now you can tilt and rotate the sensor to see the effect on the signal versus survey direction. We have found that tilt angles of 0, 45 and 90 cover all realistic installations and dip angles. Rotating the sensor often has the effect of changing the optimum direction of survey.

Try dip angle of 0 degrees with a tilt of 90 degrees (Figures 3 and 4). Try rotating 45 degrees (Figures 5 and 6). Even in a horizontal field, one can survey in both north-south and east-west directions. Geometrics sensors are fully automatic hemispheric switching allowing this versatility.

Try dip angle of 70 degrees (Indiana) with a tilt of 45 degrees and a rotation of 90 degrees (Figures 7 and 8). In some areas, maximum signal cannot be achieved in all survey directions, but any signal-to-noise lines extending out to 20 and beyond will produce excellent data in those survey directions even in turbulent air.

If you press F1 the program will identify your first available printer port and print out a laser printer compatible graphic of the screen. F2 is for Epson compatible printers. If you have both LPT1 and LPT2 operational and you want to go to LPT2, then add the following to the command line:

```
c:\csaz.exe /L=2
```

or `/L=3` for LPT3.

We welcome comments or questions. Please contact

Geometrics, Inc.
408-734-4616 tel
408-745-6131 fax
sales@geometrics.com email

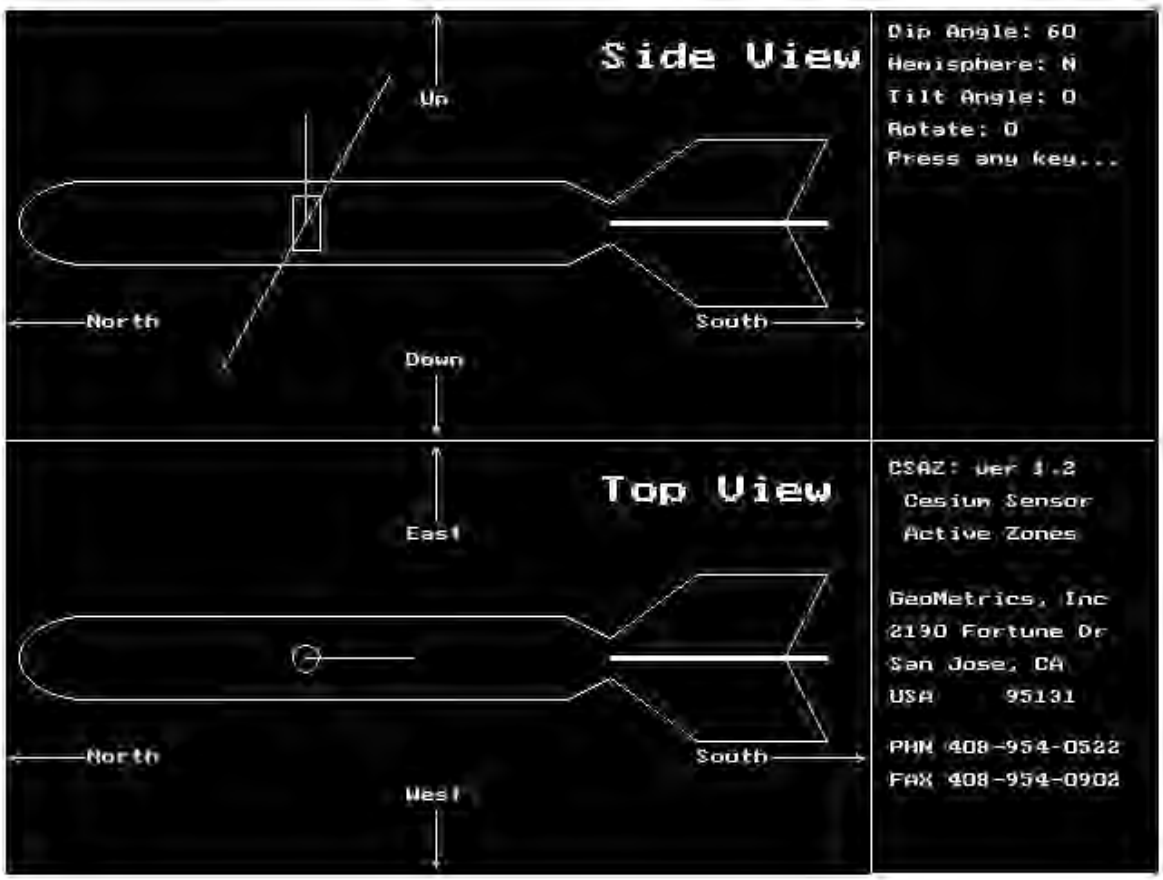

Side View
Up
North
South
Down
Dip Angle: 60
Hemisphere: N
Tilt Angle: 0
Rotate: 0
Press any key...
Top View
East
North
South
West
CSAZ: ver 1.2
Cesium Sensor
Active Zones
GeoMetrics, Inc
2190 Fortune Dr
San Jose, CA
USA 95131
PHN 408-954-0522
FAX 408-954-0902

Figure 1.

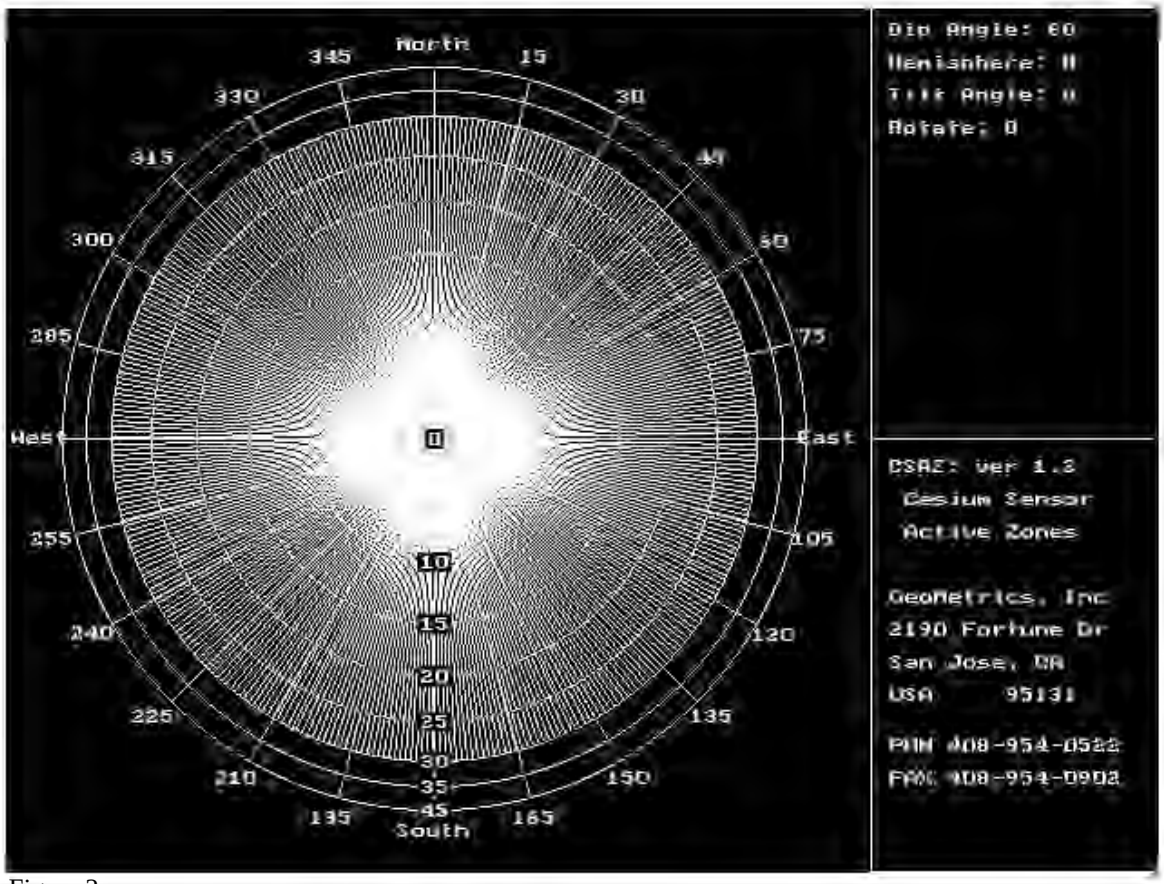

North
345
15
330
30
315
45
300
60
285
75
West
East
0
255
105
10
240
15
120
20
225
25
135
30
210
35
150
45
195
165
South
Dip Angle: 60
Hemisphere: N
Tilt Angle: 0
Rotate: 0
CSAZ: ver 1.3
Cesium Sensor
Active Zones
GeoMetrics, Inc
2190 Fortune Dr
San Jose, CA
USA 95131
PHN 408-954-0522
FAX 408-954-0902

Figure 2.

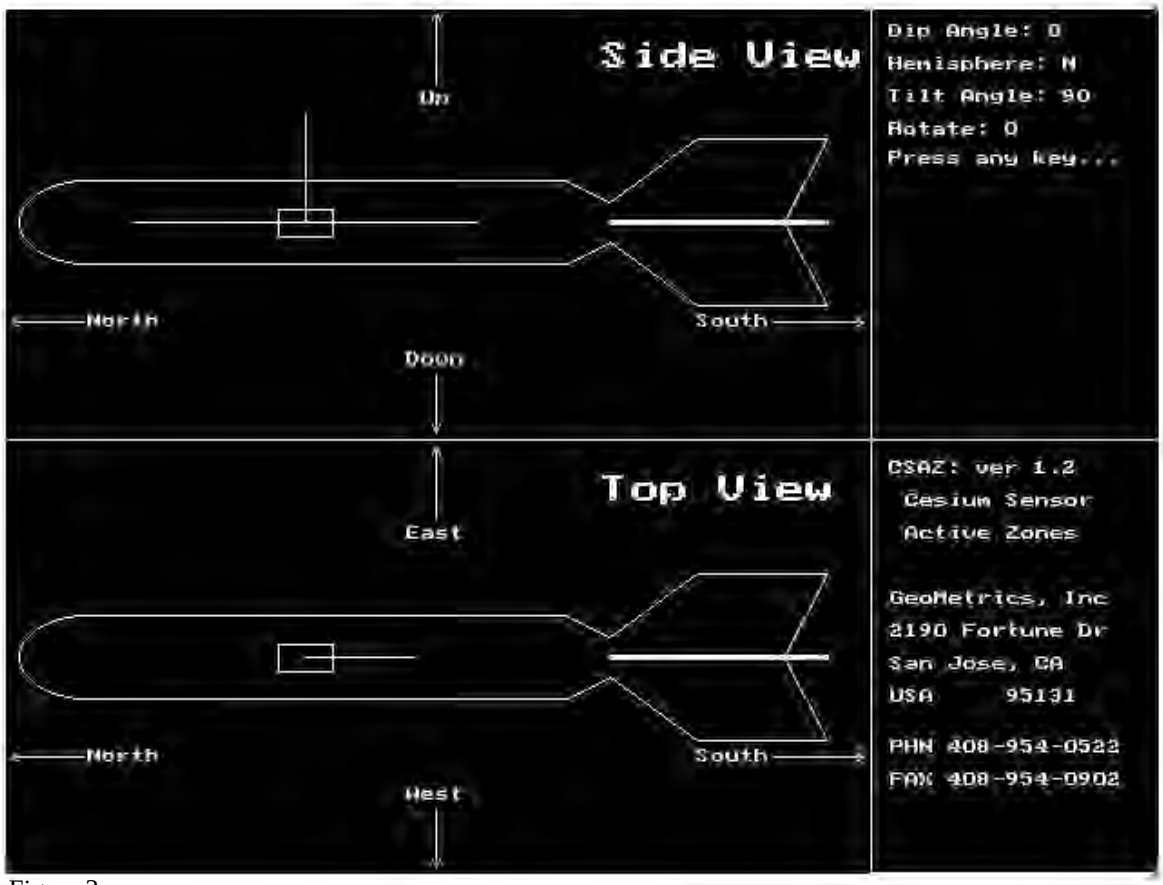

Side View
Up
North
South
Down
Dip Angle: 0
Hemisphere: N
Tilt Angle: 90
Rotate: 0
Press any key...
Top View
East
North
South
West
CSAZ: ver 1.2
Cesium Sensor
Active Zones
GeoMetrics, Inc
2190 Fortune Dr
San Jose, CA
USA 95131
PHN 408-954-0522
FAX 408-954-0902

Figure 3.

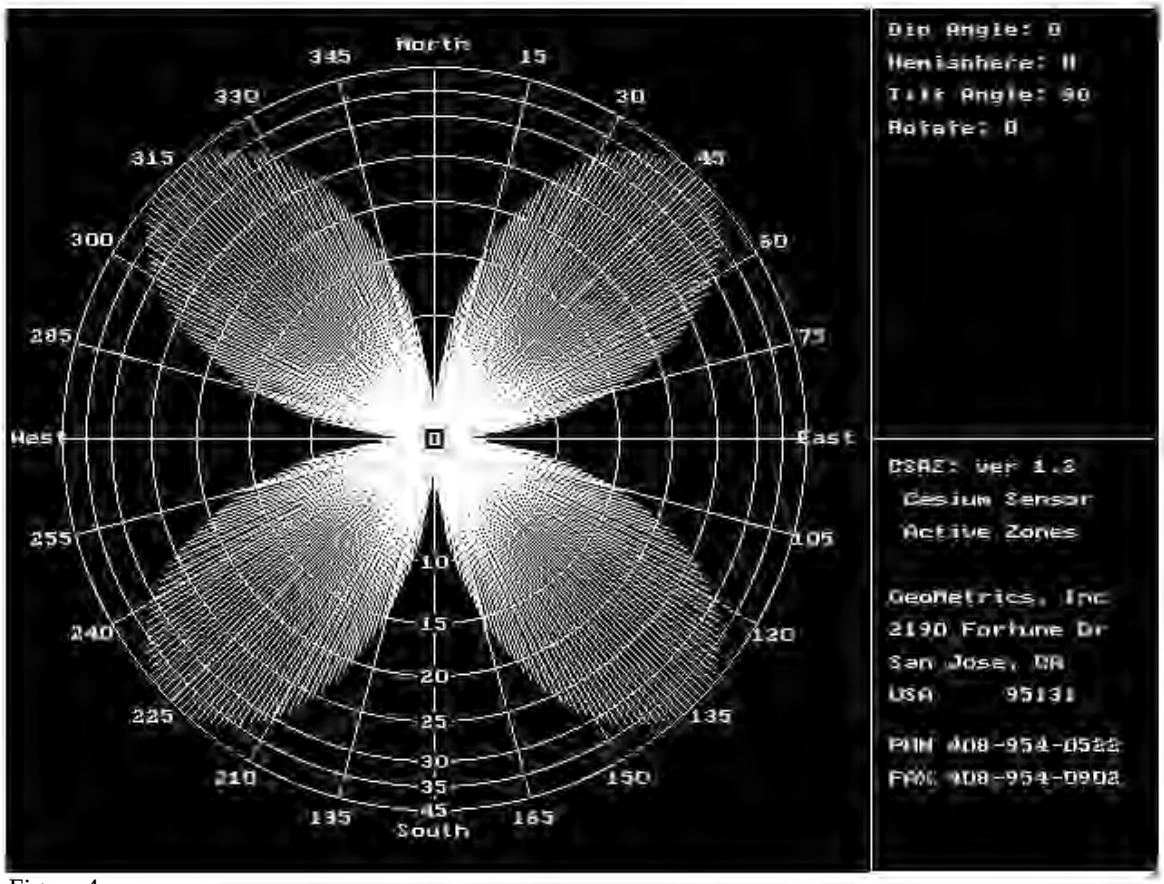

North
345
15
330
30
315
45
300
60
285
75
West
0
East
255
105
240
120
225
135
210
150
195
165
180
South
10
15
20
25
30
35
45
Dip Angle: 0
Hemisphere: N
Tilt Angle: 90
Rotate: 0
DSAZ: ver 1.3
Cesium Sensor
Active Zones
GeoMetrics, Inc
2190 Fortune Dr
San Jose, CA
USA 95131
PHN 408-954-0522
FAX 408-954-0902

Figure 4.

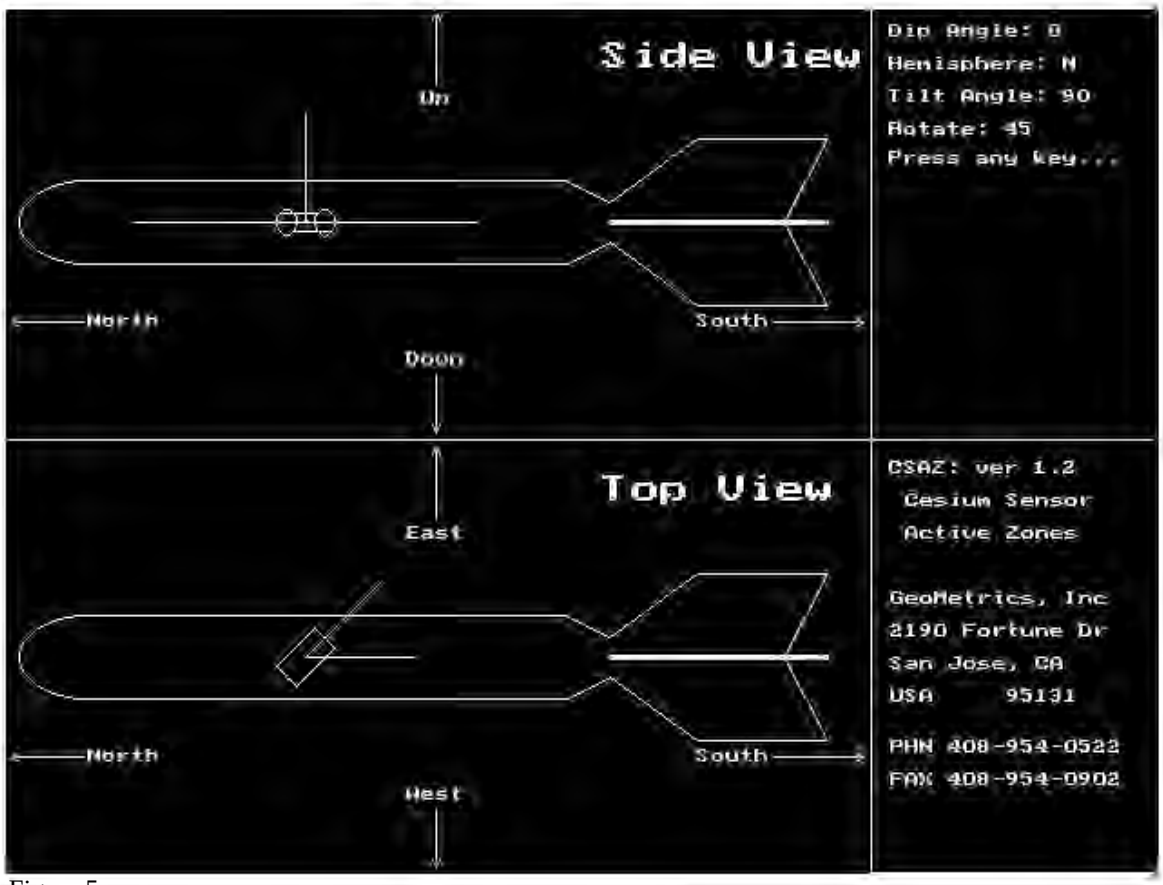

Side View
Up
North
South
Down
Dip Angle: 0
Hemisphere: N
Tilt Angle: 90
Rotate: 45
Press any key...
Top View
East
North
South
West
CSAZ: ver 1.2
Cesium Sensor
Active Zones
GeoMetrics, Inc
2190 Fortune Dr
San Jose, CA
USA 95131
PHN 408-954-0522
FAX 408-954-0902

Figure 5.

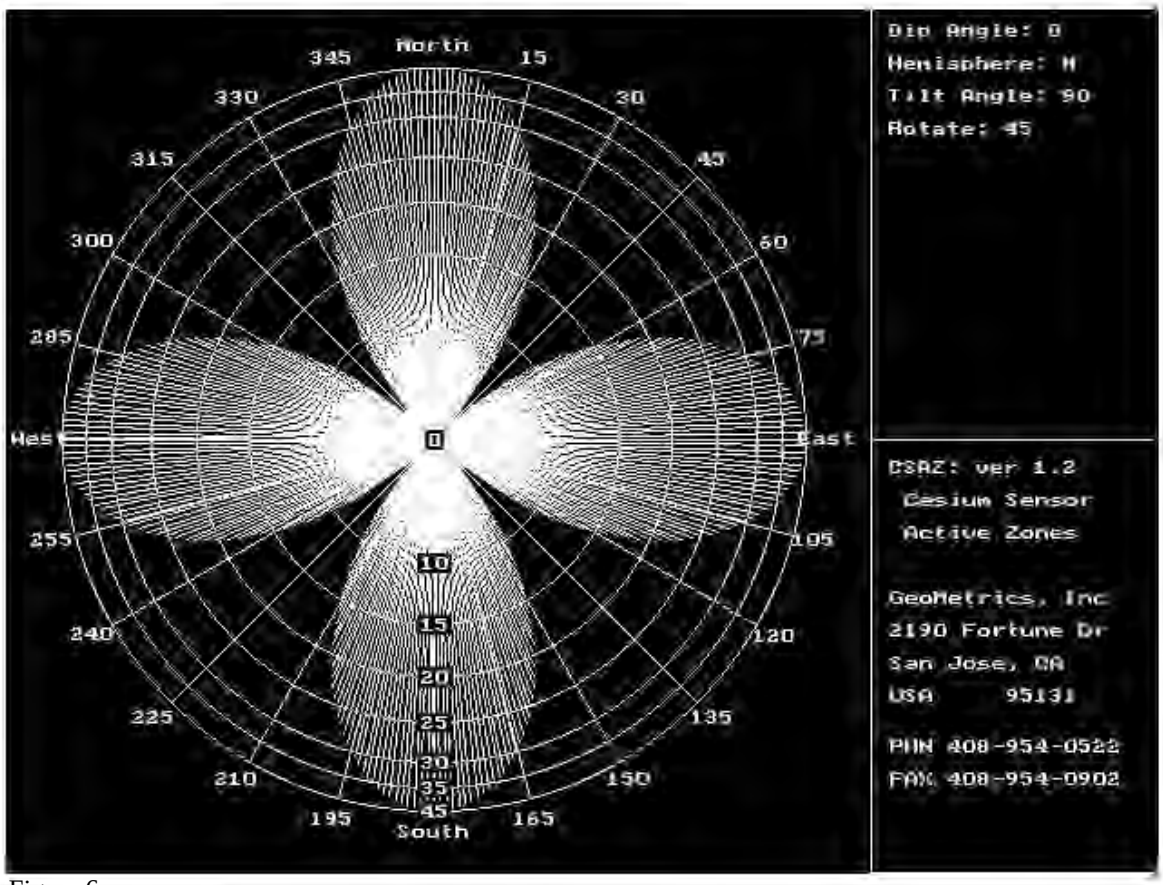

North
345
15
330
30
315
45
300
60
285
75
West
0
East
255
105
240
120
225
135
210
150
195
165
South
10
15
20
25
30
35
45
Dip Angle: 0
Hemisphere: N
Tilt Angle: 90
Rotate: 45
CSAZ: ver 1.2
Cesium Sensor
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Figure 6.

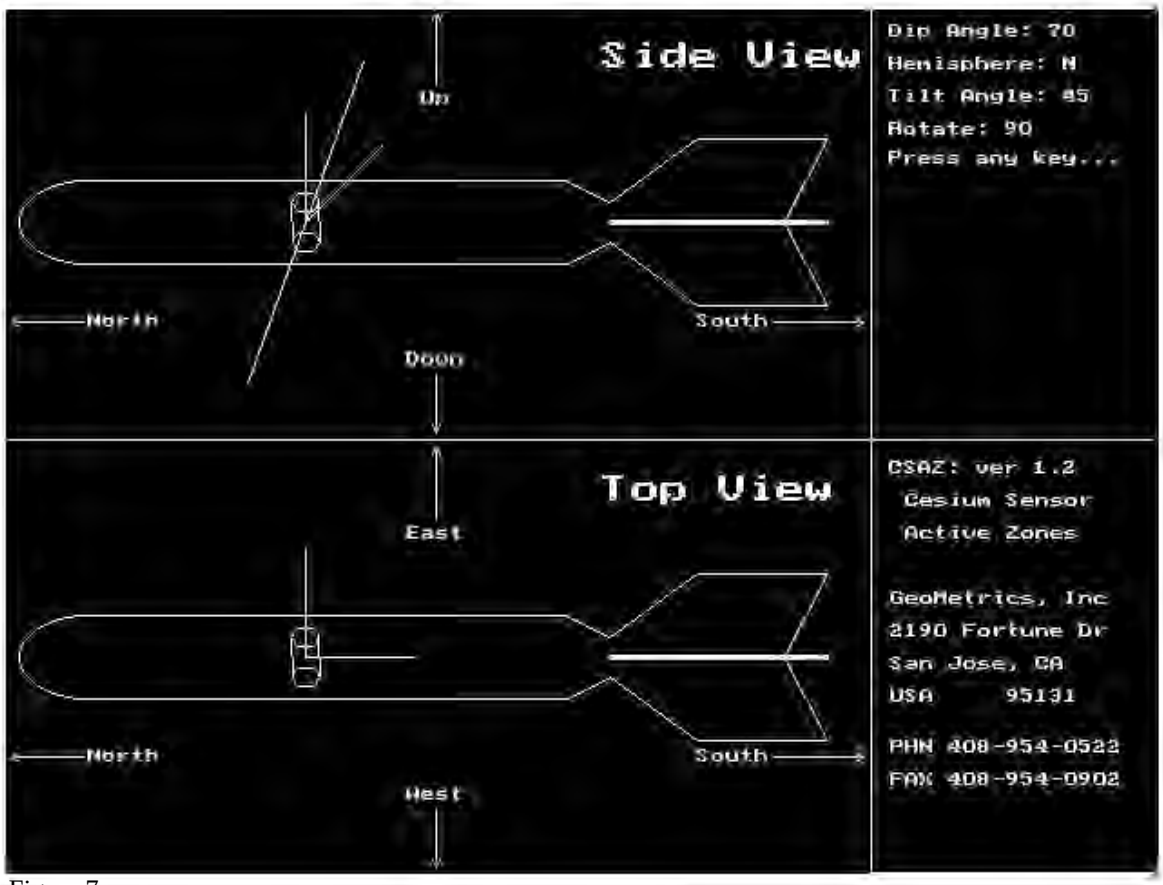

Side View
Up
North
South
Down
Dip Angle: 70
Hemisphere: N
Tilt Angle: 45
Rotate: 90
Press any key...
Top View
East
North
South
West
CSAZ: ver 1.2
Cesium Sensor
Active Zones
GeoMetrics, Inc
2190 Fortune Dr
San Jose, CA
USA 95131
PHN 408-954-0522
FAX 408-954-0902

Figure 7.

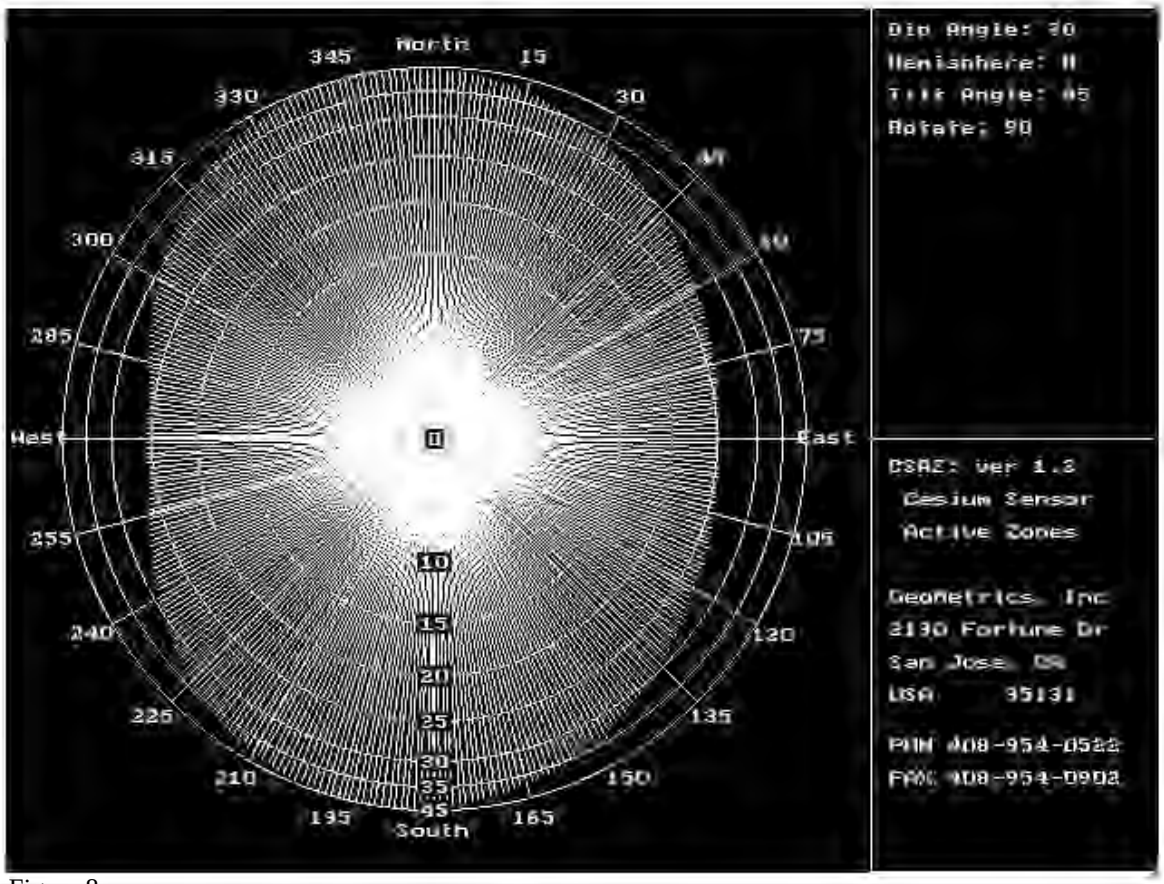

Dip Angle: 70
Hemisphere: N
Tilt Angle: 45
Rotate: 90
CSAZ: ver 1.3
Cesium Sensor
Active Zones
GeoMetrics Inc
2190 Fortune Dr
San Jose, CA
USA 95131
PHN 408-954-0522
FAX 408-954-0902
North
East
South
West
0
10
15
20
25
30
35
45
15
30
45
60
75
105
120
135
150
165
180
195
210
225
240
255
285
300
315
330
345

Figure 8

Appendix 3: Advanced Information

This information is supplied for those interested in some of the more technical aspects of the G-858. Look in this chapter for some answers to frequently-asked-questions.

Memory Usage

Inside the G-858, readings and positions (Marks and Lines) are simply stored sequentially, with a time stamp. The MagMap program will put the first reading following a mark exactly at that mark. The last reading before a Line event will be placed at that position.

Readings average about 3 bytes each, and positions about 10 bytes. GPS strings average about 30 bytes per reading. There is 1 Mbyte of memory in the standard unit, 2.5 MB in all units with the new CPU board that support 4 com ports. There is no limit to the memory used by each file.

Some memory is wasted by using additional files. Each new file must start on a 64K boundary. An average of 32K will be wasted, then, by opening each additional file.

File Formats

The following information is supplied for those users who wish to perform manipulations on the data beyond that which MagMap is capable of. This section will explain the various file formats used in the data analysis process.

Binary File

This file has the `.BIN` extension, and is a raw dump of the data contained inside the memory of the G-858. This data is not stored in a user readable format. It is compressed in a manner unique to the requirements of the operation of the G-858. Furthermore, each new revision of the G-858 firmware may cause changes in this file format. Do not attempt to modify files of this type.

ASCII File

This file has the `.STN` extension, and is in a user-readable format. This file is created by the program `BINTOASC.EXE`. This program is run with the default parameters from the MagMap program. It may also be run directly from the DOS prompt, and given many options which will adjust the format of the output. Please see the section later in this appendix describing the operation of `BINTOASC`.

The ASCII file contains lines which are a record of events from the perspective of the G-858. Events may be either magnetometer readings, MARK, END LINE, or PAUSE key presses, RS232 input strings, or field notes. Each event is recorded in the order it was received, and given a time stamp.

Note: The ASCII file lists these events backwards in time, i.e., last-in-first-out.

Each line in the ASCII file starts with a number, referred to as the TYPE in the following discussion. The TYPE indicates what information follows. The table below shows the TYPE for each of the events.

TYPE	Event
0	Magnetometer Reading
3	Position Event
6	Discontinuity Event
9	PAUSE key press
12	UNPAUSE key press
21	RS232 string
33	Field note

Positions events and discontinuities are caused by MARK or END LINE key presses. Typically, a discontinuity event is associated with the beginning of a line.

The C-program lines which `BINTOASC` uses to create these files are shown below.

TYPE 0: Magnetometer Readings

```
fprintf(pAscFile, "%-2u %10.3lf %10.3lf %.2d:%.2d:%.2d.%.2d
%.2d/%.2d/%2.d %3u\r\n",
       type,                  // 0 in this case
       reading1,              // reading from sensor 1 (front connector)
       reading2,              // reading from sensor 2
       hours,                 // time of day
       minutes,
       seconds,
       hundredths,
       month,                 // date
       day,
       year,
       status );              // G-858 internal information.
```

Example:

```
0   49881.953  49874.396 11:02:08.60 06/01/95   0
```

TYPE 3: Position events.

```
fprintf(pAscFile, "%-2u %12.2lf %12.2lf %.2d:%.2d:%.2d.%.2d
%.2d/%.2d/%2.d %10ld %11ld %11ld %3u\r\n",
       type,                  // 3 in this case
       x_position,            // X coordinate
       y_position,            // Y coordinate
       hours,                 // time of day
       minutes,
       seconds,
       hundredths,
       month,                 // date
       day,
       year,
       Number_of_Readings,    // Number of readings since last position or
                              //    discontinuity
       Line,                  // Line number
       Station,               // Mark Number
       Status );              // G-858 internal information.
```

Example: (some blanks omitted to fit onto a single line)

```
3       26.00       0.00 11:02:08.70 06/01/95      168       13      0   5
```

TYPE 6: Discontinuity events.

```
fprintf(pAscFile, "%-2u %12.2lf %12.2lf %.2d:%.2d:%.2d.%.2d
%.2d/%.2d/%2.d %10ld %11ld %11ld %3u %10ld\r\n",
       type,                   // 6 in this case
       x_position,             // X coordinate
       y_position,             // Y coordinate
       hours,                  // time of day
       minutes,
       seconds,
       hundredths,
       month,                  // date
       day,
       year,
       Number_of_Readings,     // Number of readings since last position
       Line,                   // Line number
       Station,                // Mark Number
       Status,                 // G-858 internal information.
       Positions );            // Number of positions since last discontinuity
```

Example: (some blanks omitted to fit onto a single line)

```
6       26.00       0.00 11:02:08.70 06/01/95      168       13      0   5   3
```

TYPE 9: Pause event

```
fprintf(pAscFile, "%-2u %.2d:%.2d:%.2d.%.2d %.2d/%.2d/%2.d\r\n",
       type,                   // 9 in this case
       hours,                  // time of day
       minutes,
       seconds,
       hundredths,
       month,                  // date
       day,
       year ) ;
```

Example:

```
9  18:49:44.90 05/31/95
```

TYPE 12: Unpause event

```
fprintf(pAscFile, "%-2u %.2d:%.2d:%.2d.%.2d %.2d/%.2d/%2.d\r\n",
       type,                   // 12 in this case
       hours,                  // time of day
       minutes,
       seconds,
       hundredths,
       month,                  // date
       day,
       year ) ;
```

Example:

```
12 18:49:44.90 05/31/95
```

TYPE 21: RS232 event

```
fprintf(pAscFile, "%-2u %s %.2d:%.2d:%.2d.%.2d %.2d/%.2d/%2.2d /4d%
/1d%\r\n",
       type,                   // 21 in this case
       input_string,           // ASCII string received from RS232
       hours,                  // time of day
       minutes,
       seconds,
       hundredths,
       month,                  // date
       day,
       year
       fine time               //increments of 0.25ms, set to zero every
                               0.1sec
       com ) ;                 //com port from which this data string is
                               received, 0=COM1, 1=COM2, etc.
```

Example:

```
21 $GPGGA,015009.00,3725.9975,N,12209.9992,W,2,4,002.5,00025.1,M,-
028.4,M,001,0000*65 18:49:44.90 05/31/95 0.25 0
```

TYPE 33: Field note

```
fprintf(pAscFile, "%-2u %s %.2d:%.2d:%.2d.%.2d %.2d/%.2d/%2.d\r\n",
       type,                   // 33 in this case
       input_string,           // ASCII string received from RS232
       hours,                  // time of day
       minutes,
       seconds,
       hundredths,
       month,                  // date
       day,
       year ) ;
```

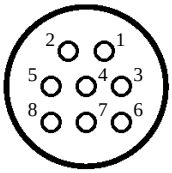
Example:

```
33 Fell down 18:49:44.90 05/31/95
```

I/O Connector Pinout

There are 3 inputs on the I/O connector which simulate END LINE, MARK and ENTER key presses. Momentarily connecting the corresponding pin to pin 4 is equivalent to pressing the key on the keypad:

I/O connector on console:

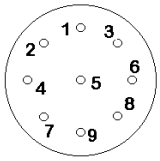


Pin Number	Function
1	Ground
2	RS232 Receive
3	RS232 Transmit
4	Ground
5	Mark
6	Audio
7	Line
8	Enter

Power Connector Pinout

If more that COM1 serial port is to be logged, COM2, COM3 and COM4 are presented on the Power Connector.

Power Connector on console:



Pin Number	Function
1	+28V
2	+28V
3	COM4-RXD
4	COM3-RXD
5	COM2-RXD
6	COM3-TXD
7	COM2-TXD
8	GROUND
9	GROUND

Some care needs to be exercised in the design of the external cables. The G858's COM1 connector's ground pin is internally connected to the ground on the power connector. If the external cables also connect COM1 connector's ground to the power connectors ground, a loop will result. This loop will appear asa shorted turn of copper wire to the EM-61. Depending on the cross section of this loop

it may effect the data from the EM-61. Also, if a substantial part of the G858's battery current finds its return path through the COM1 cable, a magnetic field will be produced. This magnetic field could effect the data when the G858 is working as a magnetometer.

We have found that building a 100 ohm resistor into the return wire of the COM1 RS232 cable prevents such problems. Simply omitting the return connection in the COM1 cable will also work, but this can cause confusion when the system is being tested, because two cables must be connected before the COM1 RS232 connections are complete.

Field Notes

You may extract the field notes into a file in much the same manner as extracting GPS data (se Chapter 9). This is done by using the BINTOASC program with options to tell it to only extract the field notes.

Type the following line at the command prompt:

```
BINTOASC input.bin output.txt -R0 -M0 -D0 -P0 -U0 -S0
```

where

input is the name of the file containing the binary downloaded data (you must type the .BIN extension

output is the filename you wish for the GPS data (you must give it an extension. The TXT extension is a suggestion, however, you may use what you wish.)

-R0 ... The options tell the program not to extract everything except the field notes. They are a dash, a letter, and the numeral zero.

You will now have created a file of the field notes, along with some G-858 formatting information. Lines will be as shown below:

```
33 Fell into a hole 10:59:14.80 06/01/95
33 Ran into a tree 11:16:25.40 06/01/95
33 Fell into a hole 12:01:36.80 06/01/95
```

Please contact Geometrics for information regarding availability of programs which automate usage of these features.

EM-61 Data

The data from the Geonics EM-61 consists of two numbers and a gain code. The new G858 software allows this data to be taken from the COM1 serial port and used in place of the magnetometer readings.

Since the numbers from the EM-61 can be both positive and negative, but the G858 software was designed for magnetic fields, which can never be negative, the EM-61 values are adjusted to make them appear in the normal range of magnetic readings. To do this, the numbers are corrected for the gain code, multiplied by 4/125 and then added to 50000.

The readings will span:

50000 - 15.000 * 32768 * 4/125 = 34271.36
50000 + 15.000 * 32767 * 4/125 = 65728.16

To convert these back to normal EM-61 values you simply calculate:

$Y = 4(X-50000)/125$

Where:
X is the reported value in nT
Y is the correct EM-61 value

MagMap2000 does not yet contain this calculation.

When using the G858 to log EM-61 data you may notice that the displayed numbers move in a more stepwise manner than it does when recording magnetic fields. This is normal. The EM-61 reports a 16 bit integer for its reading. When these are multiplied by the correct factors for each of the gains this causes the resulting values to move in increments as shown below.

15.0000 * 4/125 = 0.480
0.7500 * 4/125 = 0.024
3.7500 * 4/125 = 0.120
0.1875 * 4/125 = 0.006

SYSTEM SPECIFICATIONS

MAGNETOMETER / ELECTRONICS

Operating Principle: Self-oscillating split-beam Cesium Vapor (non-radioactive CS-133).
Operating Range: 18,000 to 95,000 nT (γ)
Operating Zones: For highest signal-to-noise ratio, the sensor long axis should be oriented at 45°, ±30° to the earth's field angle, but operation will continue through 45°, ±35°. Sensor is automatic hemisphere switching.
Sensitivity: 90% of all readings will fall within the following P-P envelopes:
0.05 nT at 0.1 sec cycle rate (SX=0.160nT)
0.03 nT at 0.2 sec cycle rate (SX=0.113nT)
0.02 nT at 0.5 sec cycle rate (SX=0.072nT)
0.01 nT at 1.0 sec cycle rate (SX=0.051nT)
Information Bandwidth: < 0.004 nT (γ)/√Hz RMS
Heading Error: < ± 0.5 nT (γ)
Temperature Drift: 0.05 nT per degree C
Gradient Tolerance: > 500 nT (γ)/inch (>20,000 nT (γ)/meter
Cycle Rate: Variable from 0.1 sec to 1 hr in 0.1 sec steps or by external trigger.
Data Storage: Non-volatile RAM with capacity for 8 hrs of Magnetometer time, event marks, location, or 3 hrs of Gradiometer and GPS at maximum sample rates.
Audio Output:
1. Audio tone of earth's field variation, pitch and volume adjustable. (Search)
2. Audio pulse each 1 second (Pace metronome).
3. Alarm for loss of signal, noise in signal (QC) or low battery.

Data I/O: RS-232 standard bidirectional serial port, selectable continuous real time data transmission via RS-232 to PC. Memory dump transfer time less than 5 min at 115Kbaud transmission rate.
Visual Output: Micro-controller driven, 320 x 200 graphic liquid-crystal display, daylight visible with selectable outputs for:
1. Data display: Up to 5 stacked profiles, real time or review mode. Map of survey grid with zoom functions.
2. All system set-up functions, e.g., memory status, data transfer, sample time.
3. All Survey set-up functions, e.g., survey profile number and direction, station or GPS number,
4. Survey monitoring functions, e.g. total field, noise level, profile number x or xy coordinates.

Internal Clock: Resolution of 0.1 sec, drift: < 1 sec/day
Power: 1.12 VDC rechargeable gel cell, 6 hrs Magnetometer or 3 hrs Gradiometer usage. Magnetic effect less than 1 nT (γ) at 3 ft.
2.Internal backup battery for clock and non-volatile RAM.
External power input 12 to 34 VDC, 1 amp on turn-on, 600ma operating in magnetometer mode.
Software: Supplied as part of the basic system for installation in the Geometrics or client-supplied PC, and including functions for:

Operating Software:
1. Survey Modes:
   a. Search
   b. Simple survey, station or continuous
   c. Map survey, station or continuous
   d. Base station
2. Data acquisition/display:
   a. Acquire and store data and survey functions.
   b. Display profiles, total field to 0.1 nT resolution, gradient (differential) to 0.1 nT, survey/map parameters and diagnostics.
   C. Map display showing location of all readings.

PC Support Software:
1. Data transfer and corrections:
   a. Transfer of data from the field Magnetometer, Gradiometer, GPS, or Base station to the PC.
   b. Diurnal correction using base station data.
   c. Processing the corrected data into ASCII values of X-Y-Z for the magnetometer and/or X-Y-Z_1-Z_2-Z_3 for the gradiometer.
2. Optional bundled "Surfer for Windows" by Golden. Provides data presentation/plotting into a contour map or 3D isomagnetic map with Text annotation and color blends.

MECHANICAL

Sensor: 2-3/8" dia., 6-3/4" long, 12 ounces 6 cm x 15 cm, 340 g
Console: 6" W, 3" H, 11" L, 3.5 lbs. (15 cm x 8 cm x 28 cm, 1.6 kg), attaches to harness. Magnetic effect less than 1 nT (γ) at 3 ft
Battery: 3" H, 5" W, 8" L, 3.5 lbs (8 cm x 13 cm x 20 cm, 1.6 kg) attaches to harness.
Staff/Harness: Staff for Magnetometer or Gradiometer, 1.5 lb to 2.5 lb (0.9 kg to 1.1 kg)
Nylon chest harness with cables attached, 2 lb to 3 lb (1 kg to 1.3 kg)

ENVIRONMENTAL

Operating Temperature: -15°C to +50°C (-13°F to + 122°F)
Storage Temperature: -35°C to + 60°C (-30°F to + 140°F)
Water Tight: To 1 ft (0.3 m) depth for 10 seconds.
Shock: Drop 3 ft on a hard surface without damage

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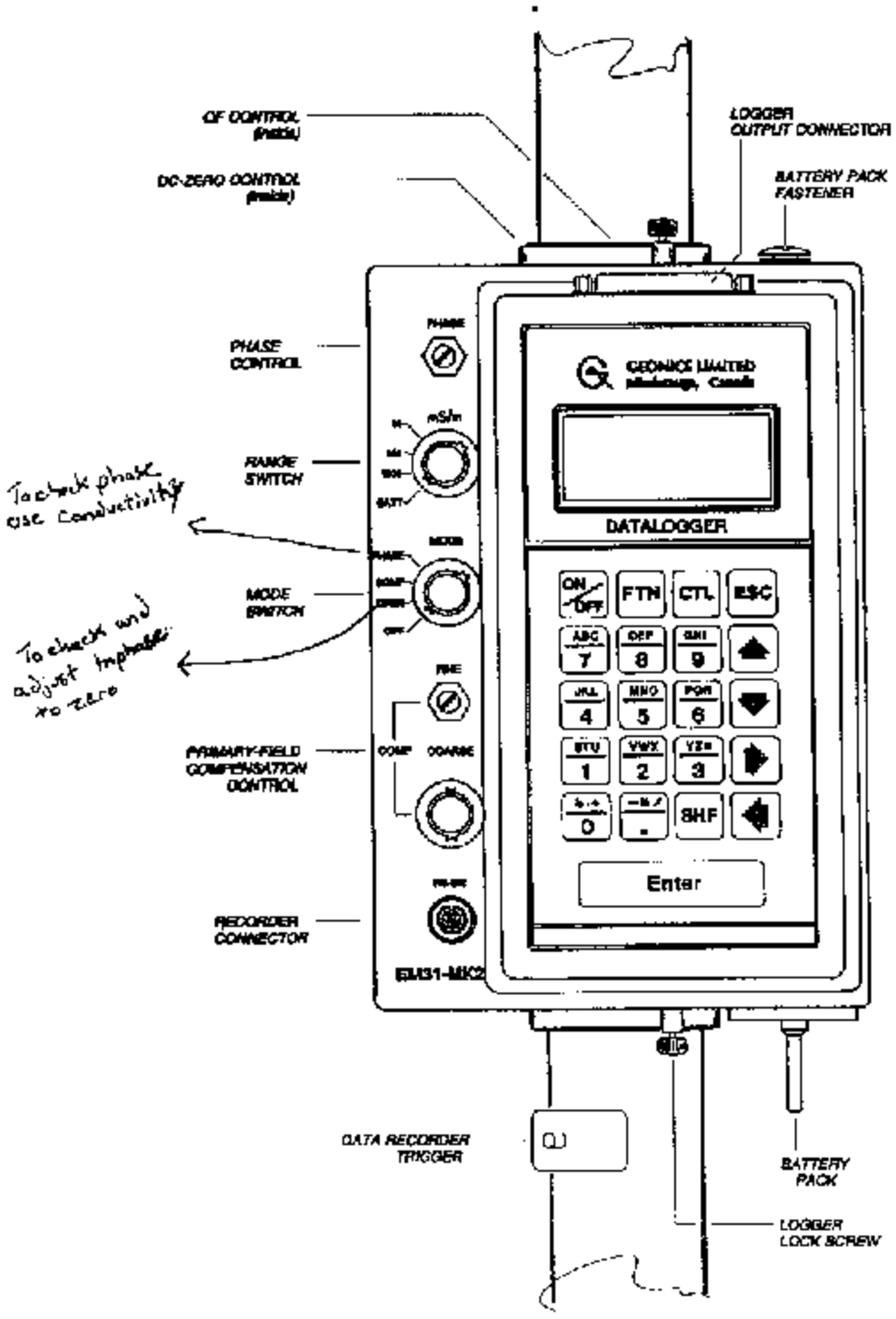


EM31-MK2 FRONT PANEL FEATURES

2.0 OPERATING INSTRUCTIONS

The EM31 can be used both to measure the electrical conductivity of the ground and to detect buried metal objects. Section 2.1 describes the procedure for measuring ground conductivity and Section 2.2 for buried metal detection.

2.1 GROUND CONDUCTIVITY MEASUREMENTS

2.1.1 Initial Set-up Procedure

a)1 Before undoing the bottom holder and releasing the transmitter and receiver coil booms, check the battery condition, plus and minus, by setting the Mode switch to the OPER position and rotate the Range switch counter-clockwise to the BATT position. Turn data logger on and run polycorder program EM31-MK2, as per EM31-MK2 data logger manual. If the display reads above ±4.4 the batteries are in good condition, otherwise replace the batteries with a fresh set of C size alkaline batteries. To get access to batteries, undo the battery pack fastener and pull the pack out of the console.

a)2 Digital Recorder (Polycorder) Batteries

- Main Batteries

The Polycorder is shipped with a special battery pack that contains six standard "AA" nickel-cadmium rechargeable batteries.

- Backup Batteries

The backup battery is a half-sized AA lithium cell. This

long life "non-replaceable" battery will maintain the Polycorder's memory for at least five years. It can be replaced if necessary, but that must be done at the factory.

- Battery Life

Ni-cad battery life with the Polycorder on the shelf is about 18 montha. Depending on the program and how efficient the operator is, battery life for fully charged batteries can be anywhere from 30 to 50 hours.

The Polycorder's operating system completely protects you from losing data because the battery hae run down. Here's how it works: as the Polycorder operates, drawing from the main supply, it monitors the batteries so that it can warn you when they need to be charged. Once battery voltage drops below a certain threshold, you will see a flashing message:

```
LOW BATTERIES
```

each time you press ESC, and each time you press ENTER while executing a program. CHARGE YOUR POLYCORDER BATTERIES AS SOON AS YOU CAN if you see this message.

If you fail to charge the batteries and voltage drops below a second threshold, the Polycorder displays the message:

CHARGE BATTERIES
CHARGE BATTERIES
CHARGE BATTERIES
CHARGE BATTERIES

Then it turns itself off and begins drawing from the backup. The polycorder "knows" not to operate on the backup battery alone. If you try to turn it on again, the polycorder immediately displays CHARGE BATTERIES and shuts down again. Hence the only demand on the backup cell is the small current required to maintain memory, which the battery can deliver for several years.

- Charging Batteries

Contrary to what you might think, it's good practice to let the main batteries discharge just short of seeing the battery messages. If you habitually recharge Ni-cad batteries when they are only slightly discharged, you will get less and less use out of each recharging. Obviously you will need to balance this with the risk of being forced to suspend data collection because the Polycorder has shut down.

The Polycorder comes with a 120 VAC battery charger. To charge the batteries, plug the charger into the Serial I/O Connector. Fully discharged batteries require 14 hours to recharge. Ni-cad batteries cannot be overcharged.

Note that the logger can be removed from the console for charging and data dumping by releasing two logger lock screws on each side of the console and pulling the logger

straight out.

- Replacing Batteries

Ni-cad batteries can be recharged several hundred times, but effective working life continually decreases. Eventually the batteries need to be replaced. It is a good practice to replace the battery pack annually.

You can change batteries without losing memory.

To replace the battery pack, turn the Polycorder off and lay it face down on a desk or table top. Loosen the six screws, pull the case bottom straight up, and lay it aside for the moment. Do <u>not</u> loosen or remove the six hex standoffs. Remove the bracket from around the battery pack. Unplug the battery connector. Remove the battery pack. Place the new battery pack in the same position as the old one. Plug in the two-pin connector. Place the bracket around the battery pack and align the six holes with the holes in the case. Drop the six outer screws in place and tighten them down. Reload program if necessary, see section II of Data Logger Operating Manual for further information on loading of the program.

b) Using the identifying labels on the tubes, select the transmitter coil tube, align it with respect to the main tube, insert it and fix it with the clamp.

c) Turn the instrument ON by setting the Mode switch to the OPER position and check the zero reading. The Range switch should be set to the least sensitive position 1,000 mS/m (this minimizes any external noise interference while checking the zero position). Tolerance for this check is ±1 mS/m on the conductivity meter. If a zero adjustment is required adjust the DC

ZERO CONTROL by using a small flat-head screwdriver to obtain a zero reading. The control could be accessed through the small hole on the side of the console box. Do not adjust Q/F control at this point.

d) Turn the instrument OFF using the MODE switch, before connecting the receiver coil, then align and connect the receiver coil tube to the main frame tube. The instrument is now ready to proceed with the functional checks.

2.1.2 Equipment Functional Checks

The Range switch should be set at 100 mS/m position for all the following tests. (If the conductivity reading is over full scale i.e., greater than 100 mS/m, see note at end of this section).

a) Set the Mode switch to the OPER position and adjust the inphase (I) reading to zero using the COARSE and FINE COMPENSATION controls. Tolerance ±0.1 ppt.

b) To check the phase of the instrument set the Mode switch to the PHASE position. Note the conductivity (Q) reading and rotate the COARSE control one step clockwise. If the conductivity reading remained the same (tolerance ±0.2), the phase is already correct; return the COARSE control to its original position (one step counter clockwise) and no further adjustment is necessary.

If there is a difference in the conductivity readings taken before and after the COARSE control was rotated one step clockwise then a phase adjustment is required. With the COARSE control in its original position adjust the PHASE potentiometer about 1/4 turn clockwise and note the new conductivity reading. Rotate the COARSE control one

step clockwise, take a reading, and return the COARSE control to its original position. If the difference in readings has decreased, repeat the procedure using a further clockwise adjustment, until rotating the COARSE control the one step clockwise produces no change in the reading. Tolerance ±0.2 mS/m.

If, on the other hand, the difference in readings has increased, the PHASE potentiometer should be rotated in a counter clockwise direction instead and the procedure described above repeated until there is no change in the readings. Always remember to set the COARSE control back to its original position. This can be confirmed by checking that the inphase (I) reads zero with the mode switch set to OPER mode. If it does not read zero, use the coarse and fine compensation controls to obtain zero on the inphase reading.

c) To check the sensitivity of the instrument, set the Mode switch to the COMP position and rotate the COARSE control clockwise one step. The conductivity reading should change between 22 to 26 mS/m. It is unlikely that the sensitivity of the instrument will vary, however, it may be useful to record the actual reading for comparison at a later date.

Return the COARSE switch to its original setting and set the mode switch to OPER. The EM31-MK2 is now ready to make ground conductivity measurements.

NOTE: a) When conducting the functional tests over ground of conductivity greater than 100 mS/m, the Range switch should be set at the 1000 mS/m range. At whatever level the Range switch is in, the reading taken in (c) should still be between 22 and 26 mS/m.

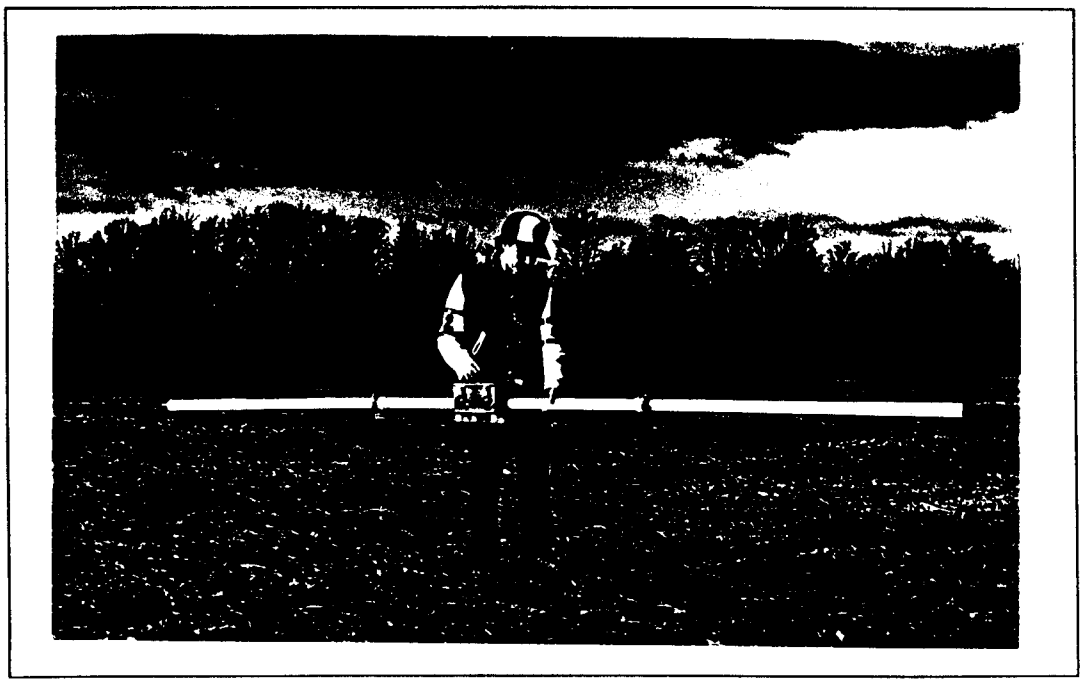
b) The maximum output range of the instrument is 20 mS/m or 200 mS/m, or 2,000 mS/m for conductivity component, and

20 ppt for inphase component.

c) At the end of the survey always remember to turn off both data logger and main console.

2.1.3 **Operating Procedure**

a) Positioning the instrument with the shoulder strap adjusted so that the instrument rests comfortably on the hip as shown, turn the Mode switch to the OPER position and rotate the Range switch so that the conductivity reads in the upper two-thirds of the full range. The conductivity display is now reading ground conductivity directly in mS/m and full scale deflection is indicated by the Range switch.



Normal Operating Position - Vertical Dipoles

b) The instrument can be operated in either of two dipole modes - vertical or horizontal (see also Section 5.3). The instrument response, as a function of depth, varies significantly between the two modes. It is important to

recognize that the vertical dipole mode provides twice the effective depth of exploration as the horizontal dipole mode - 6 m and 3 m, respectively. (A complete discussion of the vertical and horizontal dipole modes is provided in Geonics Technical Note TN-6).

When taking horizontal measurements only or both horizontal and vertical dipole measurements together the measurements should be taken at ground level.

To take the horizontal dipole measurements rotate the EM31 90° about the long axis so that the console is facing horizontally and the battery pack is on the up side.

c) When collecting discreet data points the operator can extend battery life by turning the instrument off between stations. In this case, the operator will notice a slight initial overshoot of the display at turn on. This is normal, and at least two seconds should be allowed after initial turn on before the measurement is recorded.

Alternatively, the operator may choose to leave the instrument on and watch for anomalous readings between data points. The instrument, however, has a time constant of about one second for which the operator should adjust his walking speed to obtain greatest accuracy.

Again, the effect of the instrument time constant should be recognized while logging. Fiducial marks can be placed within the data as fixed points of reference.

The orange button on the transmitter boom is used only in conjunction with the data recording systems.

It is also possible to collect data with the use of computer, by connecting the computer directly to the RS-232 output port on the EM31-MK2 front panel (with optional RS-232 interconnect cable). See DAT31-MK2 computer program manual, section 7, Real Time Logging.

2.2 BURIED METAL DETECTION

2.2.1 Set-up and Operating Procedure

The inphase component of the induced magnetic field is significantly more sensitive to large metallic objects than the quadrature phase (quad-phase) component used for ground conductivity measurements.

Typically, the EM31 inphase component will detect a single 55 gallon drum to depths of about 2 meters to the top of the drum. Under certain circumstances, however, single drums have been detected to depths of about 3.5 meters.

a) The inphase component is measured directly on the inphase (I) display with the mode switch in OPER position.

Inphase measurements are the ratio of the induced secondary magnetic field to the primary magnetic field in parts per thousand (ppt). The inphase display reads directly in ppt and it has same sensitivity regardless of the range switch position.

b) Experience has shown that the 100 mS/m range provides the optimum range setting and sensitivity for most geological backgrounds.

To carry out a survey measuring the inphase component set the Mode switch to the OPER postion and adjust the COARSE

and FINE COMPENSATION controls so that the inphase components read zero (±0.1 ppt). (It should be noted that a sudden jar to the instrument can result in a small positive or negative change in the reference level).

The lack of a true zero reference should not cause any serious difficulty or confusion with interpretation since metal targets are generally recognized by anomaly signatures in the data.

As an example, Figure 3 shows typical inphase or quad-phase response when the instrument is carried over a metallic pipeline. Variabilty in the shape, depth and orientation of the target will alter the shape of the anomaly. These anomalies can be characterized by increasing or decreasing, and possibly negative values or some combination of each.

NOTE: It is always advisable, when surveying for buried metal to record both the inphase and quad-phase components. While the inphase, in general, is a better detector of metal, the quad-phase is more sensitive to long, extended targets (eg. pipelines) which are, at least partially, in electrical contact with the ground.

3.0 INSTRUMENT CALIBRATION

Prior to shipping, the instrument is calibrated in the factory to read properly. If necessary, calibration procedures are easily carried out as described below. **IMPORTANT** - The most critical adjustment is the QF (quadrature fine) potentiometer which has been precisely adjusted at the factory.

Before any adjustments are made it is strongly recommended that the instrument first be set up at a fixed height over a known location and the ground conductivity carefully noted. If this adjustment is misaligned the instrument will have to be recalibrated over ground of known conductivity.

3.1 Null Calibration

The zero setting of the EM31 can be readily set by following the procedure described in Section 2.1.1 (c).

3.2 Absolute Calibration

Absolute instrument calibration is easily achieved if any area of ground is available of known and constant conductivity down to the depth of penetration of the instrument. The procedure is simple; the instrument is located over the known area at ground level and the QF compensation control is adjusted until the meter reads 1.12 times the correct terrain conductivity. If the ground conductivity is high, Figure 2 must be used to correctly set the instrument reading.

It is wise to maintain such an area as a calibration check area even if the variation of the conductivity with depth at that area is not accurately known. This is useful for cross checking with future measurements.

NOTE: The QF and NULL controls are located under the front panel. Battery pack must be removed to gain access.

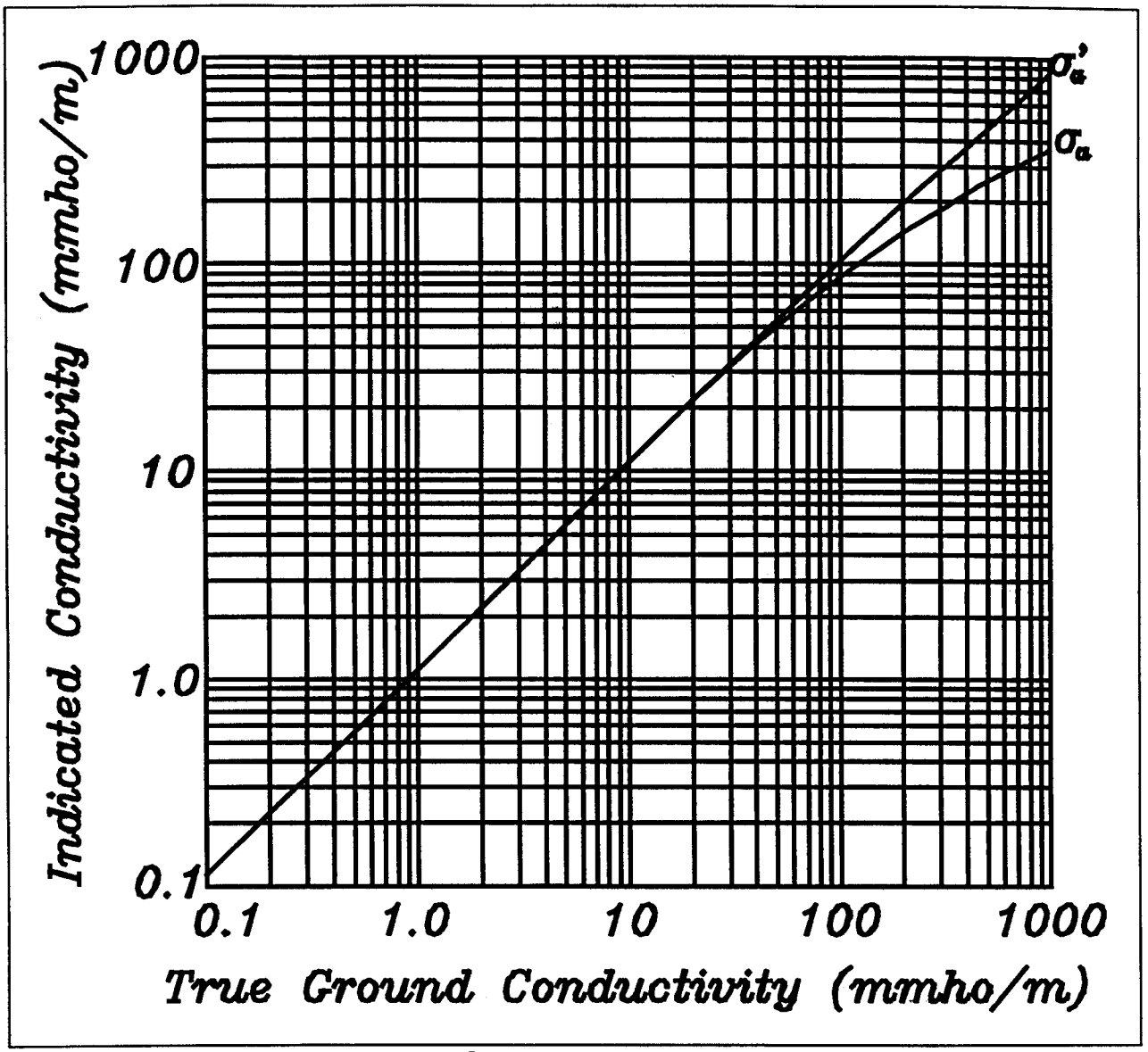


Figure 2: *Conductivity Correction: Instrument on the ground surface*

4.0 SURVEY TECHNIQUE

Surveying with the EM31 is straightforward. As pointed out in 2.1.3. (c) measurements may be made either continuously or on a station-by-station basis. In either case it is always recommended, as for any other geophysical survey, that survey lines and measurement stations be carefully laid out, and the survey performed in a systematic fashion with the resulting data accurately plotted for each measurement station. The most common survey error is to have the survey lines too short, in which case they do not extend sufficiently far off the expected anomalous region to permit the operator to establish the background values of terrain conductivity.

The decision as to the correct spacing will be based on a knowledge of the lateral dimension of the anticipated resistivity anomaly. To ensure the correct spacing, it is useful at the start of the survey to continuously observe the conductivity values that are encountered as the operator moves along the survey line.

The resolution in conductivity of the EM31 is also high, with changes of 5% being quickly perceived. This instrument is capable of giving an extremely precise survey with information on small variations in the terrain.

It was seen in Section 1 that current flow within the earth consists of a series of concentric circles, assuming that the conductivity is laterally uniform. Therefore, in the case of a uniform half-space, rotation of the instrument in a horizontal plane about the transmitter coil as a pivot will produce no change in the meter reading. Conversely, any change in the reading as this procedure is carried out is an indication of lateral inhomogeneities in conductivity. It is simpler and usually sufficiently accurate for the operator to rotate the instrument through 90° using himself as pivot

4.0 **SURVEY TECHNIQUE** (cont'd)

at each measurement station. Thus if the lines are in a north-south direction the operator would normally walk along the line with the instrument pointing in a north-south direction; at each measurement station he can also take a reading with the instrument pointing east-west to check that this is essentially the same as the north-south reading. In the event that this reading is significantly different it may be worthwhile for the operator to then rotate the instrument to the points where the conductivity reading is both a maximum and a minimum, and to record both values. The average value can then be used for the data reduction.

The EM31 is sensitive to underground conductors such as large pipes, drums, etc. These are usually easily recognized by the large meter fluctuations which occur within a short distance, as shown in Figure 3. The negative going peak indicates the location of the pipe. It is then possible to accurately determine the location and strike the direction (azimuth) of the conductor axis as follows: the approximate location is determined as above, and a traverse is then made over the conductor with the EM31 pointing in the approximate direction of the conductor axis. The meter reading will now be a positive maximum when the instrument is both directly over the conductor **and** pointing accurately along the conductor axis.

The instrument is relatively unaffected by fences, overhead power lines, and other nearby metallic objects. In order to determine whether the reading is influenced by such structures the operator should rotate the instrument to check for changes in reading, becoming suspicious if a maximum or minimum occurs when the instrument points either perpendicular or parallel to the structure. Before recording the measurement the operator should move away from the structure until no evidence of lateral inhomogeneity is seen when the instrument is rotated.

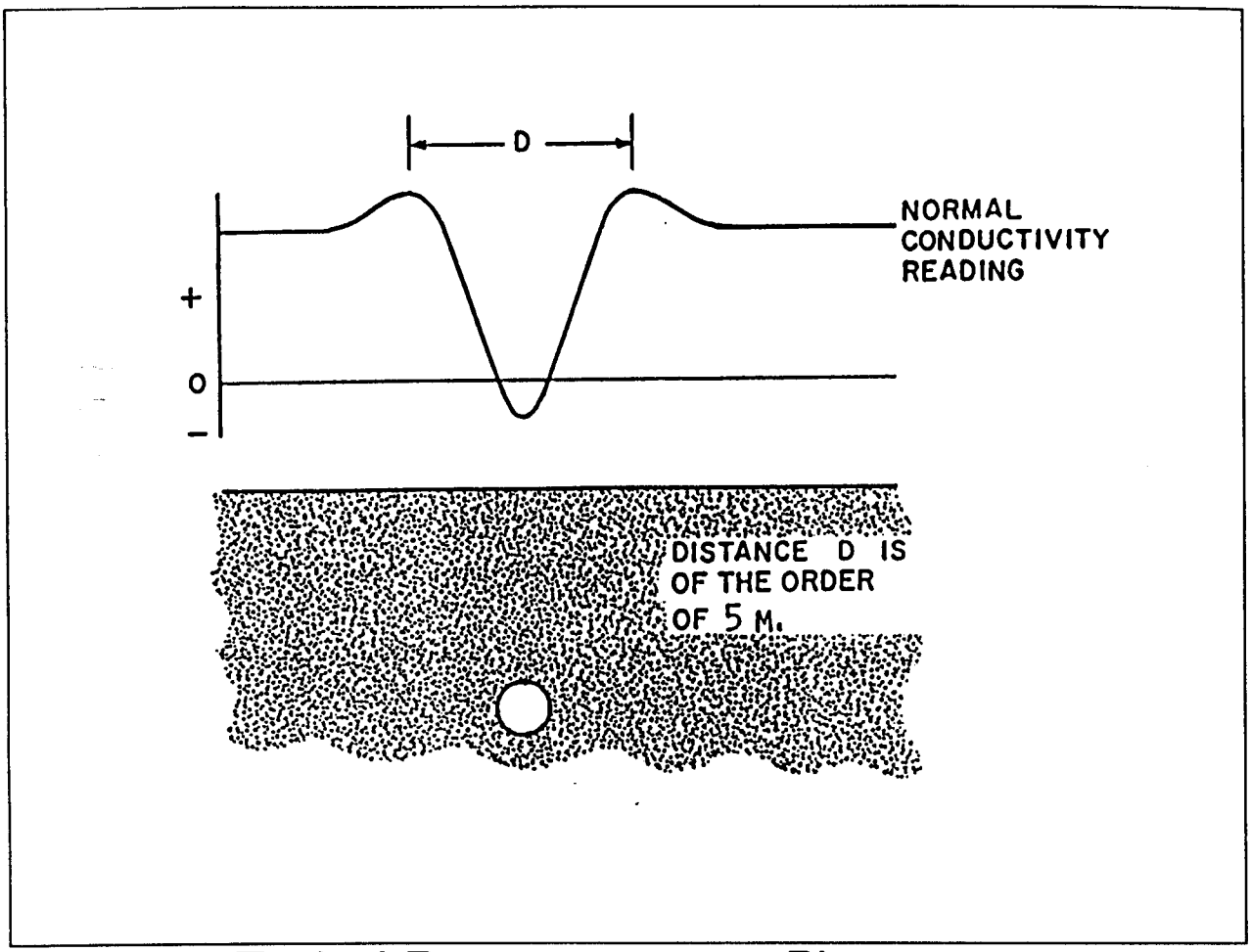


***Figure 3**: Typical Response over a Pipe*

4.0 **SURVEY TECHNIQUE** (cont'd)

It should be remembered that the EM31 is an electromagnetic tool and care should be taken near obvious conductors until the operator has satisfied himself as to their possible effect. In every case this is determined by rotating the instrument and determining whether there is a maximum and minimum which appears to be related to the structure. If a structure is giving such an effect it is not advisable to take the average value of the two readings as in an indicator of the terrain conductivity.

4.0 **SURVEY TECHNIQUE** (cont'd)

In general the conductivity readings obtained with the EM31 will vary smoothly from one region to another. In some cases, however, as for example where a well defined vertical contact separates a poor conductor from a very good conductor, edge effects may be seen in which the readings vary rapidly with position and are no longer a good indicator of the terrain conductivity. Edge effects may also occur where a very good conductor (a few ohm-meters or less) has dimensions of the order of the intercoil spacing, and again the indicated readings may not accurately reflect the true terrain conductivity. In any circumstance where the apparent conductivity varies significantly in a distance which is short compared with the intercoil spacing the possible presence of edge effects or local subsurface conductors must be considered.

Finally, particularly during mid-summer afternoon, electrical static (electromagnetic radiation from local or distant thunderstorms) may cause the meter readings to become noisy. This is usually evidenced by sudden flicks of the meter display, however, in very severe cases the meter display may simply wander about an average reading. Should this occur it is recommended that measurements cease until the "spherics" are over, usually later in the afternoon. Similarly, noisy readings may also be noted when making measurements near large power lines.

OPERATING INSTRUCTIONS

DAS70/31 DATA LOGGING SYSTEM
FOR FIELD COMPUTERS Pro4000 and Allegro

EM31pro

Version 1.23

May, 2003

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Table of Contents

1. Introduction

The Geonics EM31pro Data Logging System (DAS70/31) consists of a field computer Allegro or Pro4000, data logging program EM31alg or EM31pro, and associated cable to connect the Allegro or Pro4000 to the Geonics EM31-MK2 instrument. The program EM31alg is designed for the Allegro field computer, although, if necessary it can be used with any other IBM compatible computer running a MS DOS operating system and equipped with serial port. The only disadvantage of using a standard laptop computer, will be small size of the display which is limited for the Allegro. This documentation describes the use of the EM31pro program used with the Pro4000 field computer, and the Geonics EM31-MK2.

The program EM31pro records data together with a time stamp at each station. Data files created with this program can be used to position a survey according to locations recorded separately by a Global Positioning System (GPS).

The EM31pro will also accept NMEA-0183 compatible data from a GPS receiver directly connected to a Pro4000 field computer. GPS data which are embedded in the EM31pro data file can be processed later in the Geonics DAT31W program. The connected GPS must be able to stream NMEA-0183 compatible messages. The EM31pro uses two NMEA messages GGA and GSA. While message GGA is mandatory, the GSA string is used only to provide information related to the GPS signal quality.

Program EM31pro acquires and records survey data from the EM31-MK2 system, under the control of the operator. It also records various field information such as survey line number (line name), starting station, increment, comments, etc. Readings can be displayed in text or graphic mode. Readings are displayed in real time in mS/m or ppt. In addition, the program allows you to monitor the instrument output while data are not recorded. The EM31pro also continuously monitors the EM31 measured component (Conductivity and Inphase), dipole mode (Vertical or Horizontal), instrument scale (10, 100 or 1000), state of fiducial marker, as well as GPS signal quality parameters (if connected to the system) without leaving the program.

The program allows the user to set the EM31pro into a specific instrument mode of operation: AUTO, Wheel, or Manual modes. In AUTO mode readings can be automatically recorded in desired time intervals. In Wheel mode readings are triggered by a counter installed at the wheel assembly, and in MANUAL mode readings are triggered manually by the operator. In AUTO and Wheel modes the program can record one combination of the EM31 component (Conductivity and Inphase, or Inphase in COMP mode) and dipole mode (Vertical or Horizontal) per station. In Manual mode any combination of dipole modes can be taken at each station, and data can be averaged at up to 99 samples per reading.

Survey setup parameters are saved in a file, therefore they can be automatically used during subsequent data collection sessions. In addition, ten preset survey setups are provided. These setups are user selectable, they can be edited and saved for future use.

In addition to logging EM31-MK2 data, the EM31pro provides data file management tasks. The program allows you to upload data files to a PC running the DAT31W program. It also has options allowing viewing and deleting data files. Data files are always saved to the programs current directory. Data file names, which can be set by the program based on the computer clock or they are user specified, have extension names R31.

Over 350,000 readings can be collected in the field computer Pro4000 with the standard memory of 8 Mb. The maximum speed of data collection is approximately 10 readings per second in text mode, and 9 readings per second in graphic display mode. In graphic display mode, the profile containing the last 84 (or 140 in Allegro) data readings for each channel is displayed.

2. Program Requirements

To successfully use this software, you will need :

Computer

Field computer Pro4000 or Allegro

or alternatively:

- IBM PC and compatibles,
- Minimum 640 Kbytes of available memory,
- DOS 3.1 or higher,
- Floppy drive or other mean to transfer files,
- CGA graphics capability,
- One Serial Port
- optionally, Two Serial Ports if directly connected GPS system is to be used.

Geonics EM31-MK2

The EM31-MK2 instrument with associated cables.

2.1 Contents of EM31pro disk

The program EM31pro is stored on one 3.5" floppy disk. All necessary initial files (with extension names .INI) are created in your computer after the program is run for the first time. Check that the file EM31pro.EXE is included on the floppy disk.

3. Installing EM31pro

While using the Pro4000, Allegro, or other field computer which is not equipped with a floppy drive disk, the EM31pro.EXE file should be transferred from a PC computer using software and serial cable provided by manufacturer.

On other computers the EM31pro program can be installed by copying the EM31pro.EXE file to a directory on your hard disk. This can be performed by using Windows Explorer or at DOS prompt (described below). It is assumed that A: indicates floppy drive, and C: indicates hard disk drive.

A directory (i.e. EM31) can be created with the command MD from DOS.

C:\MD EM31

In order to access directory EM31, type:

C:\CD EM31

Once in EM31 directory the EM31pro.EXE file can be copied from the distribution disk.

C:\EM31\ COPY A:EM31pro.EXE

After you run the program for the first time it will create permanent initial files EM31pro.INI, SURVEY0.INI, SURVEY1.INI, etc. which contain some of the program settings. If the above files do not exist on the default drive they will be created with default parameters during the first execution of the program.

The EM31pro data files with extension name R31 will be created in the program current directory.

4. Running EM31pro Program

The EM31pro is a menu-driven program designed to be simple to use.

Most of the menus contains (from the top):

- name of the menu,
- informative window (instrument type, file name, etc.),
- list of options and parameters,
- list of available commands.

Menu selections are made using the **Up**/**Down** arrow keys. The selected option is highlighted and can be executed by pressing <**ENTER**> key.

Left and **Right** arrow keys are used to edit selected parameter. When editing **Up** or **Down** arrow keys can be used to exit current parameter.

The carriage return key is described as <**ENTER**>, <**CR**>, or symbol. Where permitted by the program, the <**Esc**> key is used to quit the current menu and return to the former one.

In general, settings for most menus can be saved by the function key **F1**. The function key **F2** is used to cancel editing and to return to former settings.

While using the Pro4000 field computer the program can be started from the ProShell utility program by selecting its name. Otherwise, the program is started from a copy on the working disk, by entering the name EM31pro in response to the DOS prompt, i.e.:

C:\EM31**EM31pro** <CR>

While using the Pro4000 ProShell DOS utility or FileScout DOS File Manager in Allegro Field PC, the computer system will prompt for parameters. Since there is no parameters required press simply <**ENTER**> key.

After name EM31pro is entered, the menu, presented in the next section and afterwards called MAIN MENU, is displayed.

5. Main Menu

The Main Menu appears always as the first menu after the program is started. It contains the name of the program, its version number, and list of available options. The EM31pro Main Menu is displayed below.

These options are selected by using the **Down** and **Up** arrow keys. Use **<ENTER>** to execute the highlighted item. Short description for each of the options follows.

5.1 Short description of Main menu options

Monitoring

This option allows to monitor the EM31 instrument output.

Acquiring Data

Executing this option leads to the Data Acquiring Menu which allows to set up survey options and logging parameters.

Setup Logger

Menu that is associated with this option is used to set the date and time of the computer, audio click, serial port number, type of pause key, and type of display (text or graphic).

Set Port for GPS

This menu allows to disable and enable GPS data acquisition. This menu is also used to set the serial port number used for GPS input, and to specify necessary serial port communication settings.

Upload Files

This option allows to upload recorded data files to a PC computer running DAT31W program.

View Files

The program will display list of available data files that can be reviewed.

Delete Files

This option allows to delete permanently not needed data files from the field computer disk.

Exit

Selecting this option will terminate the program execution.

6. Monitoring

The Monitoring menu allows initial inspection of the range of the instrument readings at the particular site, monitoring the instrument performance, and quick inspection of the instrument settings.

It is assumed that the instrument is turned ON prior to using this option. In case the instrument is OFF or the instrument console is not connected to the computer the following message will appear:

Check the connection or turn the instrument ON and select the Monitoring option again.

Assuming that the instrument works properly the program will display Monitoring menu and will start displaying instrument readings. At this stage the layout of the Monitoring menu is as follows:

The EM31 readings are updated approximately 10 times per second during monitoring session. Values of conductivity in mS/m and Inphase in ppt are displayed. The dipole mode, instrument scale, and state of fiducial marker are continuously updated.

When GPS was Disabled in the Set Port for GPS menu a message GPS Disabled will be displayed. If the GPS port is Enabled and a working GPS system is connected to the field computer the Monitoring screen will display a few more parameters, as presented below.

In the above Figure one line of the display is dedicated to show the GPS status. A label **DGPS** (Differential Global Positioning System) indicates that GPS readings are differentially corrected in real time, while label **AGPS** (Autonomous Global Positioning System) indicates lack of differential correction. On the right side of **DGPS** or **AGPS** label small square is displayed. This square should move down and up with the frequency of GPS update rate (usually 1 second intervals). If the square is not moving for long periods of time it means that the GPS system is not working or that it is not connected to the field computer. The next label **P** with a value varying between 0 and 99.9 represents an index called Position Dilution of Precision (**PDOP**). The last label **S** and following number shows number of currently tracked satellites. Refer to section 9 (Set Port for GPS), Appendix A, and to GPS manuals for more information about GPS parameters.

To exit the Monitoring option press the function key **F2**.

7. Logger Setup Menu

This option allows you to set several parameters in the logger. The Logger Set Up menu is presented below.

Description of Parameters:

Date

This option allows you to change the date in the field computer clock. When the option is highlighted pressing the **ENTER**, or **Left** or **Right** arrow keys, enables editor that allows the operator to change day, month and year.

The new date is accepted (and set in the computer) after the function key **F1** is pressed.

Use **Down** or **Up** arrow key to exit the editor and cancel any changes.

Time

This option allows you to change time of the day in the field computer clock. When this option is highlighted pressing the **ENTER**, or **Left** or **Right** arrow keys, enables editor that allows the operator to change hour, minute, and second.

The modified time is accepted (and set in the computer clock) after the function key **F1** is pressed.

Use **Down** or **Up** arrow key to exit the editor and cancel any changes.

Units

Two selections are available: **Meters** or **Feet**.

COM Port

The number of serial port that is assigned to the EM38RT. Available selections: COM1 and COM 2. The program default is COM1. Communication parameters for the selected serial port are set by the program, since the EM31-MK2 operates only at Baud Rate (9600), Parity (N), Data Bits (8), and Bit Stop (1).

This port must be different than the port specified in the Set Port for GPS menu (see next), otherwise a message will be displayed and ports will have to be reassigned.

The serial port selected here is also used for uploading data files to the PC.

Audio

Two selections are available: **Yes** or **No**. The audible click will be generated at each reading when this option is enabled.

Pause key

Three selections are available: **Any key**, **Alt+F1**, and **Ctrl+F5**. This feature is used to pause data recording during logging session. Default setting **Any key** can be changed to one of the two key combinations for field conditions where a logger key can be accidentally pushed causing unwanted stop of data logging.

Display

This parameter specifies the display type during data collection. Two types of display can be selected: Text mode or Graphic mode.

In the text mode conductivity and Inphase data are displayed in digital form. This mode is recommended for instrument AUTO mode when the highest possible frequency of data collection is used. The same applies to Wheel mode since the data triggering can be accelerated at any given moment (while passing a curb, downhill, etc.).

The graphic mode allows to display profiles for any selected reading (combination of component and dipole mode) in real time as well as simultaneous display of readings in digital form for all measured data. When the Display Graphic is selected, four additional parameters are activated (see menu below).

Parameter **Cond V** (conductivity in vertical dipole mode), **Cond H** (conductivity in horizontal dipole mode), and similarly for Inphase component **Inph V** and **Inph H** allow you to enable (Yes) or disable (No) display of each type of reading separately.

Regardless of which combinations are chosen, data for all types of readings will be displayed in digital form below profile display.

After all the parameters in the Logger Setup menu are updated press the function key **F1** to accept the displayed settings. The program will return to the Main menu.

To return to the original settings (state before this option was selected) press the function key **F2**. All parameters will be reset to the initial settings and the program will return to the Main menu.

8. Set Port for GPS Menu

After the Set Port for GPS option is selected in the Main Menu the Set Port for GPS menu appears on the screen. This menu allows you to enable and disable the GPS input, specify serial communication parameters matching GPS receiver settings, and to monitor the GPS output in terminal mode (key F3). The menu is presented below.

GPS Input

This option allows you to Enable/Disable a serial port for GPS input. When Disabled is chosen logging and monitoring screens will display message "GPS disabled" in place of GPS parameters.

The GPS Input can be Enabled even if there is no GPS system connected to the Pro4000. In such case data file will contain proper sequence of EM31-MK2 readings without any GPS input.

COM Port

The number of serial port that is assigned to the GPS input. Available selections: COM1 and COM 2. The program default is COM2. Communication parameters for the selected serial port can be determined in options described below.

This port must be different than the port specified in the Logger Set Up menu (for EM31-MK2), otherwise a message will be displayed and ports will have to be reassigned.

Baud Rate

Specify Baud Rate for the output port, the entered value should much the Baud Rate of the GPS system, default is 9600.

Parity

Select Parity for the output port, the entered parameter should much the Parity set in the GPS serial port settings, default is N.

Data Bits

Specify Data Bits for the output port, the entered value should much settings in the GPS system, default is 8.

Stop Bits

Specify Stop Bits for the output port, the entered value should much settings in the GPS system, default is 1.

After all the parameters in the Logger Setup menu are updated press the function key **F1** to accept the displayed settings. The program will return to the Main menu.

To return to the original settings (state before this option was selected) press the function key **F2**. All parameters will be reset to the initial settings and the program will return to the Main menu.

To activate terminal mode which allows you to monitor GPS receiver output press the function key **F3**. The monitoring mode will work regardless of the GPS Input being Enabled or Disabled. This option is described in the following section.

8.1 Monitoring GPS Receiver Output

After the function key F3 is pressed in Set Port for GPS menu the program will display the screen in terminal mode. In this mode the screen is divided into three parts. The top portion of the screen, labeled Receive GPS Data, displays the GPS receiver output. The middle portion labeled NMEA Command is used to enter NMEA commands to be sent to the GPS receiver, and at the bottom, the screen menu with available options is displayed. This screen is shown below.

As soon as the EM31pro screen is in terminal mode and the GPS is streaming data, the first 20 characters of each message will appear in the top portion of the display. The display is updated with the frequency the GPS receiver outputs data. This allows you to recognize the GPS update rate and type of messages being sent by the connected GPS. In cases where the GPS data is not received by the logger a message NO DATA and current time will appear in the top window of the display, as shown below.

The message NO DATA is normally updated with a rate of 6 seconds. This may indicate the following: serial port number not correctly specified in Set Port for GPS menu, GPS receiver not sending any data, and not working or not connected GPS receiver. If the message is updated more often than 6 seconds (i.e. every 1 or 2 seconds) or the display doeas not show legible characters, it is possible that the GPS is working correctly and is connected to the proper serial port, however communication parameters are not specified correctly. In most cases the Baud Rate or Parity must be adjusted.

The NO DATA message may also appear if the GPS data are received correctly, but the GPS receiver was set to send data with a time interval longer than 6 seconds. In this case the NO DATA message will be displayed in between GPS messages. This indicates that the GPS is working correctly, however the operator should consider adjustment of the GPS receiver output update rate. Most high resolution geophysical surveys require positioning update of 1 or 2 seconds, and a 5 seconds interval can be used only when the survey is carried out at an even pace and along relatively straight survey lines.

The monitoring display can be stopped any time by pressing the function key **F1** (labeled **Stop**). At that time scrolling of the GPS output will be stopped, and the function key **F1** will be labeled **Go**. The next pressing of this key will activate receiving and display of GPS data.

8.2 Sending NMEA Messages to GPS Receiver

The function key F2 allows you to send a NMEA command to the GPS receiver. It is preferable if the GPS receiver parameters are set using the GPS manufacturer software or controller (GPS logger or panel keys). However, **when the operator is familiar with NMEA protocol and structure of commands for a given GPS system**, this function can be very convenient and useful when the update rate and enabling or disabling messages in the data stream is required.

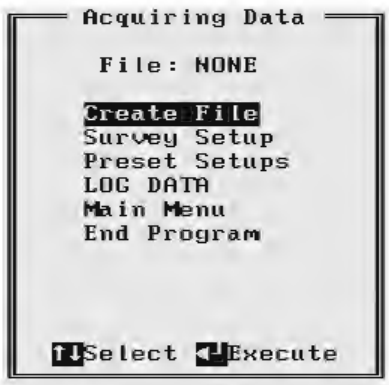
After the function key **F2** is pressed the portion of the screen labeled NMEA Command is activated and the beginning of the standard NMEA command, **$PASHS,** is displayed. After the entire NMEA command is typed in, press the key **<ENTER>** to send the command to the GPS receiver. Pressing the <Esc> key will cancel the command and deactivate the NMEA Command window. An example of a command that will remove the NMEA message **SAT** is given in the below figure (it is assumed that the GPS receiver output serial port is A).

After this command is reived by the GPS receiver, the confirmation message will be send by the receiver ($PASHR, ACK*3D) and data stream will not contain the message SAT ($PASHR, SAT,..... in the above figure).

Please note, that not every GPS system accepts and uses the same standard set of NMEA commands and messages. In addition, some GPS systems do not accept commands sent by the serial port at all. The configuration of these type of receivers can be updated only by the controlling device (usually GPS logger, controllel, or the receiver panel keys). An example of the latter is widely used GPS Trimble ProXRS.

9. Acquiring Data Menu and Logging

After the Acquiring Data option is selected in the Main Menu the Acquiring Data menu appears on the screen. This menu is presented below.



At the top of the screen the current name of the data file is displayed. If data file is not created its name is displayed as NONE. The menu contains several options listed below.

Create File

This option creates data file.

Survey Setup

The Survey Setup menu will be displayed. Instrument mode and survey settings can be specified in this menu.

Preset Setups

List of 10 predesigned survey setups will be displayed. Each survey setup can be edited and saved by the user for later use.

LOG DATA

This option is used for actual monitoring and logging EM31 data.

Main Menu

The program returns to the EM31pro Main Menu.

End Program

Executing this option will end the program.

9.1 Create File Menu

The Create File option can be executed before or after the Survey Setup parameters are specified.

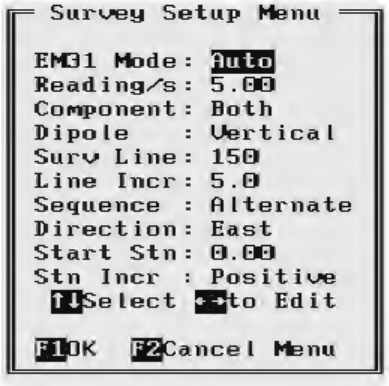
The log file is created in the current directory (containing the EM31pro program). The name of the file is given by the field computer clock and it consists of month (2 digits), day (2 digits), hour (2 digits), and one alphabetic character A, B, C, etc. (If all letters during one hour are used use the Overwrite option). The Create File menu is presented below.

The file can be created by pressing the function key **F1**, this option can be skipped by pressing the function key **F2**., or by pressing key **F3** the file name can be overwritten. After key **F3** is pressed the Create File menu will be displayed as follows.

Each data file in the field computer (raw data file) has an extension name R31 and it is created in the programs current directory. The R31 files are created in the instrument binary format. They can be viewed using the Main menu option "View Files". These files can be also converted to ASCII format and processed in the Geonics program DAT31W and DAT31 (for DOS).

9.2 Survey Setup Menu

The Survey Setup menu, presented below, contains several parameters which affect two important procedures: instrument settings (instrument mode, frequency of data collection, etc.) and survey geometry layout (survey line names, line spacing, start station, station increment, etc.).



To select any option use the **Down** and **Up** keys. To start the editing of any setting press **Left** or **Right** key. Some parameters that have only a few possible options (e.g. EM31 Mode) can be simply toggled by **Left** or **Right** keys.

Description of the Survey Setup menu options and parameters.

EM31 Mode

Set the EM31 mode of operation by pressing **Left** or **Right** arrow keys. Available modes are: Auto, Wheel, and Manual. These modes of operation are described below.

Auto Mode

Readings will be triggered automatically at a specified frequency (see option Readings/s).

In Auto Mode only one component (conductivity or Inphase) and one dipole mode (Vertical or Horizontal) can be selected.

Please note that when Auto mode is selected, parameter Wheel Inc. or Samp/Rdg are not available, see figure above. At the same time the Stn Incr (station increment) has only two options: Positive or Negative.

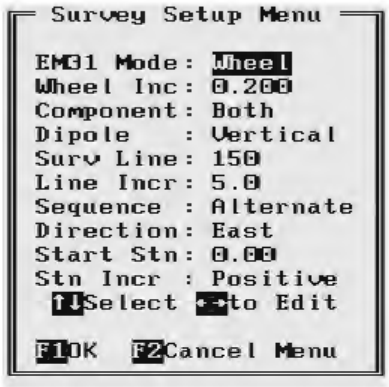
Wheel Mode

This mode is available only if the system is equipped with adapted (i.e. EM61) wheels.

Readings will be triggered automatically by a counter attached to the wheel.

In Wheel Mode only one component (conductivity or Inphase) and one dipole mode (Vertical or Horizontal) can be selected.

Please note that when Wheel mode is selected the option Reading/s or Samp/Rdg are not available, see figure below. At the same time the station increment (Stn Incr) has only two options: Positive or Negative.



Manual Mode

Readings will be taken only while the manual trigger (switch on the instrument consol or a handle) is pressed.

In Wheel Mode any combination of components (conductivity and Inphase) and dipole modes (Vertical and Horizontal) can be selected.

Please note that when Manual mode is selected options Wheel Inc. and Reading/s are not available. In this mode any value can be entered for the station increment (Stn Incr) parameter.

Readings/s

When this option is highlighted the editor is activated and you can enter desired value. The editor accepts only numerical values.

This parameter describes number of readings per second that will be taken. Any number larger than zero can be entered, however the EM31 maximum frequency of data output is 10 readings per second.

At high frequencies (above 5 readings per second) obtained frequency may slightly differ from the specified rate, however speed of data collection will be consistent for a given field computer. The real speed of data collection (in Auto mode) depends on the field computer used and display type. In general, displaying data in the text mode allows for faster data collection and while using fast computers the difference between specified and obtained frequency is very small.

This parameter is displayed only when the Auto Mode was selected.

Use **Down** or **Up** arrow key to leave editor.

Wheel Inc.

When this option is highlighted the editor is activated and you can enter desired value. The editor accepts only numerical values.

In case the EM61 or EM61-MK2 wheel assembly is adopted to EM31 system a wheel increment is approximately 20 cm (or 0.64 feet). If the Hand Held EM61-MK2 wheels are used then two wheel increments 0.1 and 0.2 m are available. Check the wheel increment setting on the antenna assembly.

This option is displayed only when the Wheel mode was selected.

Use **Down** or **Up** arrow key to leave editor.

Samp/Rdg (Samples per Reading)

When this option is highlighted the editor is activated and you can enter desired value. The editor accepts only numerical positive values.

This parameter describes number of readings that will be taken after the trigger switch is pressed. At the end of sampling time the logger will beep and an average value will be written in to the file and plotted on the screen. During the sampling period interval data are measured at approximately 10 readings per second. For example by specifying 10 samples, 1 second will be used at each station. The maximal sampling is 99 readings which corresponds to approximately 10 seconds at each station.

This option could be used to improve quality of data in areas of high industrial noise, especially if the ground conductivity is relatively low (small response signal).

In cases when multiple sampling is not required (good signal to noise ratio) enter the value **0** or **1** and 1 reading per station will be taken.

This parameter is displayed only when the Manual Mode was selected.

Use **Down** or **Up** arrow key to leave editor.

Component

When this option is highlighted press **Left** or **Right** to toggle between two available settings: Both and Inphase.

When Both is selected two EM31 components will be displayed and recorded: Conductivity and Inphase.

Please note, if Both setting is used, a switch on the instrument panel must be set to OPER mode and if Inphase is selected the same switch must be set to COMP mode.

Use **Down** or **Up** arrow key to leave editor.

Dipole (instrument dipole mode)

When this option is highlighted press **Left** or **Right** to toggle between two or three available settings: Vertical, Horizontal, and Both.

When Manual mode was selected three settings are available: Vertical, Horizontal, and Both. If Auto or Wheel mode was selected two available dipole modes are: Vertical or Horizontal.

Use **Down** or **Up** arrow key to leave editor.

Surv Line (survey line name)

When this option is highlighted press **Left** or **Right** arrow key to activate editor and then enter desired value. Use **Down** or **Up** arrow key to leave editor.

This is a user's tag number/name for the profile line. The length of the name can not exceed 8 characters. The line name is usually used as a coordinate perpendicular to the survey lines direction. For example, when survey lines are laid out along W-E direction stations describe W-E coordinate, while Line names may describe S-N (vertical on a map) coordinate.

Line Incr. (survey line name)

When this option is highlighted press **Left** or **Right** arrow key to activate editor and then enter desired value.

This parameter specifies the distance by which survey lines will be separated. This setting will be used to determine number (name) of the next survey line.

Use **Down** or **Up** arrow key to leave editor.

Sequence

When this option is highlighted press **Left** or **Right** to toggle between two available settings: Alternate and One Way.

Alternate is used when neighboring lines are surveyed in the opposite direction, which is the most common procedure during field surveys.

One Way is used when each survey line is traversed in the same direction.

The choice of this parameter will affect the default start station, a signature of the station increment, and line direction when parameters for the next survey lines is determined.

Direction

When this option is highlighted press **Left** or **Right** to toggle between four available settings: East, West, South, and North.

This parameter indicates the heading of the survey line.

Use **Down** or **Up** arrow key to leave editor.

Start Stn (start station of a survey line)

When this option is highlighted press **Left** or **Right** arrow key to activate editor and then enter desired value.

This parameter specifies the starting station number for the selected survey line. This value is used in conjunction with Station Increment to calculate the current station number for display purposes.

Use **Down** or **Up** arrow key to leave editor.

Stn Incr (station increment)

When this option is highlighted press **Left** or **Right** arrow key to activate editor.

In case the EM31 Manual mode was selected enter desired value for the station increment. If Auto or Wheel modes were selected then, the **Left** and **Right** arrow keys will toggle between two available options: Positive and Negative.

This parameter specifies the station increment for the selected survey line. This value is used in conjunction with Start Station to calculate the current station number for display purposes.

In Auto mode the increment is assumed +1 (Positive) or -1 (Negative), while in Wheel mode it will be Positive or Negative value of the specified Wheel Increment.

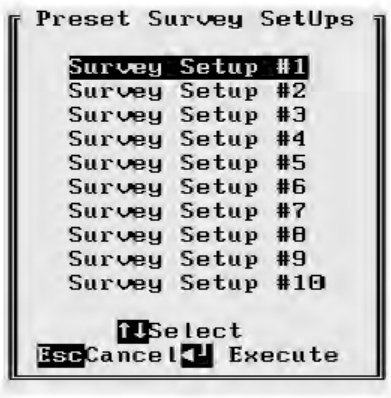
Use **Down** or **Up** arrow key to leave editor.

After all the parameters in the Survey Setup menu are updated press the function key **F1** to accept the displayed settings. The program will return to the Acquiring Data menu. Updated settings will be written to the initial file and they will be given as default parameters in the subsequent Survey Setup menu display.

To return to original settings (state before this option was selected) press the function key **F2**. All parameters will be reset to initial settings and the program will return to the Acquiring Data menu.

9.3 Survey Setups

The Preset Survey Setups menu, presented below, contains list of ten predesigned Survey Setup. Each Survey Setup can be configured and saved by the user for subsequent use. As a default surveys 1 to 4 are assigned for various settings of survey conducted in EM31 Auto mode, and surveys 5 to 10 contain various settings for EM31 Manual mode.



To select any survey set up number use **Down** and **Up** keys, and to start editing particular Survey Setup menu press <**ENTER**>. Press <**Esc**> key. to return to the Acquiring Data menu.

After a Survey Setup number (e.g. Survey Set Up #2) is selected the following screen will appear:

The survey parameters are updated in the exactly same way as in the Survey Setup menu (see section 9.2).

After all parameters are specified three options represented by function keys **F1**, **F2**, and **F3** are available :

F1 (OK)

The display returns to Acquiring Data menu. The selection will become the current Survey Setup parameters, however settings will not be saved as a Survey Setup # for subsequent use.

F2 (Cancel)

The display returns to Acquiring Data menu. The selection is cancelled and it will not be saved.

F3 (Save)

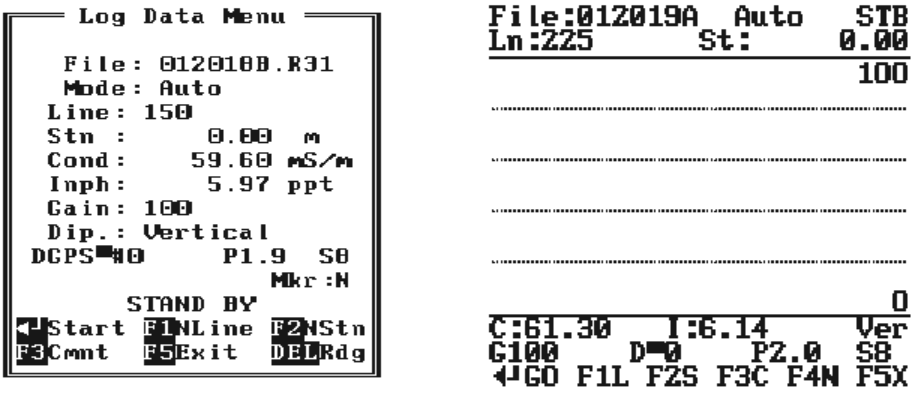
The selection is saved as a particular Survey Setup number. The display does not return to Acquiring Data menu, nor it becomes the current Survey Setup. In order to use the edited parameters as a current Survey Setup use function key **F1**.

9.4 LOG DATA Menu

After the Acquiring Data menu option LOG DATA is highlighted press <**ENTER**> key. It is assumed that the instrument is turned ON prior to using this option. In case instrument is OFF or the instrument console is not connected to the field computer the message shown below will appear.

Check the connection or turn the instrument ON and select the LOG DATA option again.

Assuming that the instrument works properly and the LOG DATA is selected in Acquiring Data the program will display Log Data screen. The layout of the Log Data screen depends on the type of the display selected in the Logger Set Up menu. The Log Data menus have two display modes, the text mode (on the left) and the graphic mode (on the right) are presented below.

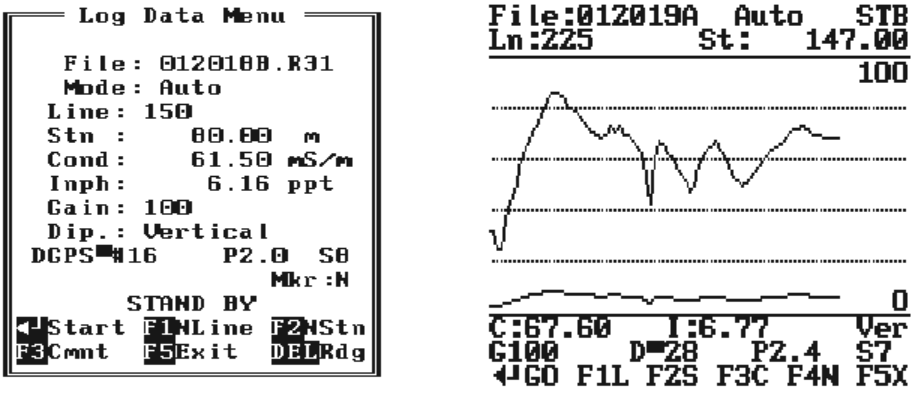


Regardless of the display type the Log Data menus have two operating modes: Stand By and Logging. In the Stand By mode the EM31 data and the instrument settings are monitored with the update rate of approximately 10 times per second. In this mode the operator can monitor the instrument output (without recording the data), the component, instrument dipole mode, instrument scale, GPS parameters (if Enabled), as well as change the operation to the Logging mode, and access several field options. In the Logging mode when the EM31 data is recorded in the data file, field options can not be accessed.

When the Log Data menu is displayed for the first time it appears always in the Stand By mode.

Stand By Mode

The Log Data menus have two display modes, the text mode (on the left) and the graphic mode (on the right) are presented below.

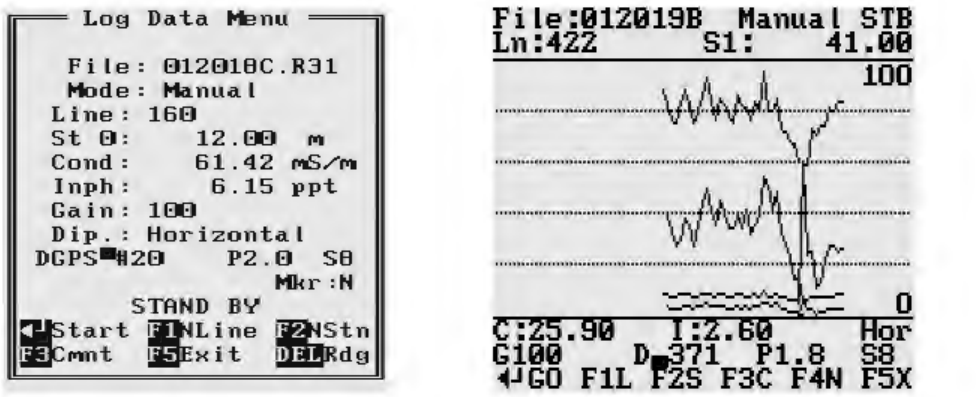


The main portion of the screen in graphic mode is occupied by the plot area. Readings in the plot area can be displayed in the user specified scale. The amplitude scale is divided by four or five dotted grid lines. In cases where the amplitude scale starts with a negative value, then the grid line corresponding to zero is always plotted as a solid line.

Readings for conductivity or Inphase are shown in digital form in the central portion of the screen in the text mode, and below plot area in the graphic mode. In graphic mode due to small screen of Pro4000 readings are labeled C for conductivity and I for Inphase. Units (mS/m and ppt) are not displayed in the graphic mode.

Both modes show the log file name and optional GPS parameters. Name of the Log Data menu mode is displayed in the text mode, and it is shown as an abbreviation in the top right corner of the screen in graphic mode, STB for Stand By mode, and LOG for logging mode. The instrument component setting, the instrument gain (G in graphic mode), and dipole mode (labeled Ver or Hor in graphic mode) are updated continuously in both modes. When the fiducial marker is pressed a label M will appear on the screen in graphic mode, and Y will be displayed at label Mkr in the text mode..

Current survey line name and station number is displayed at the top of the screen. In the Stand By mode the station number will not change. Stations in the EM31pro program are incremented by 1 or station increment value after each reading is written to the data file. If more than one readings are taken at the same station, available only in Manual mode, station is incremented after necessary number of readings is taken. In the latter case number of readings taken at the given station is displayed in the field following label S (and in front of current station), as shown in Figure below..

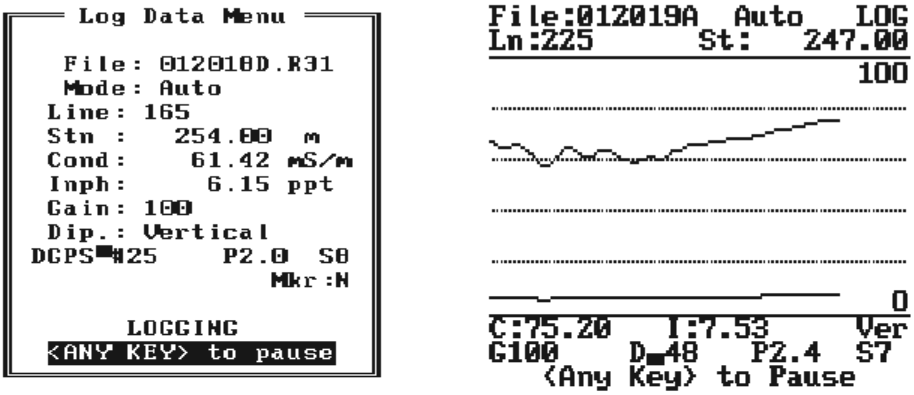


Similarly, the stations with the GPS readings (assuming that the GPS is connected to the logger) remain the same in the Stand By mode. Number of GPS positions is incremented by 1 after each GPS reading is written to the data file. In the text mode number of GPS positions follows label **DGPS** (or **AGPS** positions are not differentially corrected), the corresponding label in graphic mode is **D** (or **A**). Small square moving up and down in Stand By mode indicates that the GPS system is monitored and it is working. Two other GPS parameters: PDOP (represented by label **P**) and Number of Tracked Satellites (label **S**) are updated continuously in Stand By mode.

Several available field options are listed at the bottom of the Stand By mode screen. They will be described in the following section 9.5.

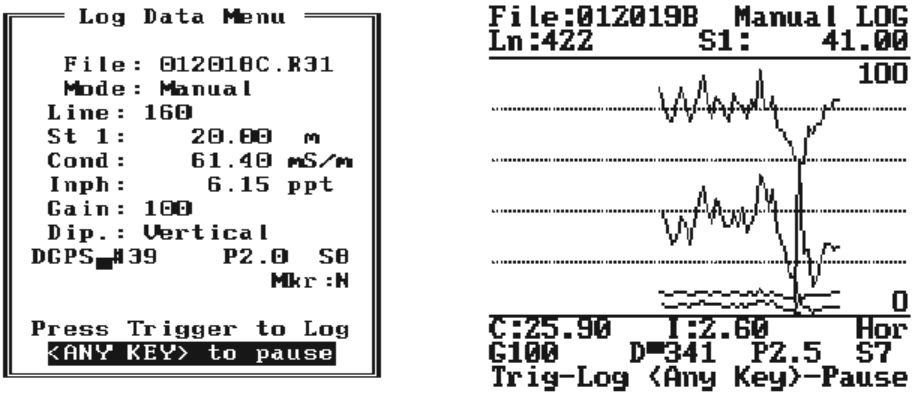
Logging Mode

The Logging mode is enabled by pressing the <**ENTER**> key, which corresponds to label **Start** in the Text Display, and **GO** in the Graphic display mode. After this key is pressed the bottom portion of the screen will change and data will be logged in the mode corresponding to the selected EM31 mode in the Survey Setup menu. Log Data screens in logging mode in the text (on the left) and graphic (on the right) display modes (for EM31 Auto mode) are presented below.



After the screen changes to Logging mode current station (**Stn** in Text and **St** in Graphic display mode) is updated according to the station interval. Similarly, if GPS Input was enabled, total number of GPS positions in the data file is incremented every time (usually once a second) GPS position is written to the file. If the Graphic display mode is enabled profiles (or profile) curves are updated after each reading is written to the data file. The program displays profiles for readings that were selected in the Logger Setup Menu and at the same time they correspond to selection in Survey Setup menu (component and dipole mode). If the latter condition is not met readings will be saved in the file and displayed in digital form, however corresponding profile will not appear on the screen. The audible click sounds at each reading if Sound option was enabled in the Setup Logger menu.

Log Data screens in logging mode in the text (on the left) and graphic (on the right) display modes (for EM31 Manual mode with 2 readings per station) are presented below.



There is only one option available in the Logging mode - pause logging. After a Pause key (any key, Alt+F1, or Ctrl+F5) selected in Logger Setup menu is pressed the recording is stopped and the Log Data menu returns to the Stand By mode. The EM31 data will be displayed with the update rate approximately 10 readings per second, however data will not be saved in the log file, audible click will stop if Sound option was enabled, and if graphic mode is used, profile curves will not be updated.

Exit from the logging session and access to field options are available only from the Log Data menu in the Stand By mode.

9.5 Field Options

Several field options are available while the Log Data screen is in the Stand By mode. These options are listed at the bottom of the screen.

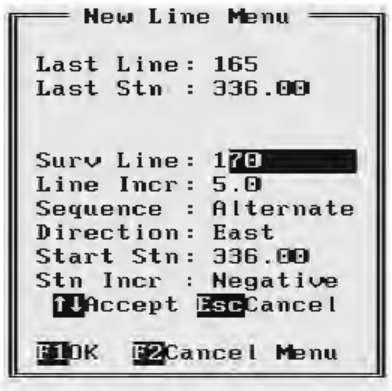
<ENTER>

This option is labeled **Start** in the Text display mode, and **GO** in the Graphic display mode. The Log Data screen changes from Stand By to Logging.

F1 (New Line)

This option is labeled **NLine** in the Text display mode, and **L** in the Graphic display mode. The New Line menu is displayed, which is the same for Text and Graphic display modes.

Selecting this option allows the operator to enter a new survey line number (name) and associated information (Direction, Start Station, and Station Increment). The new line number and associated parameters will be prompted by the program based on parameters specified in the Survey Setup menu.



At the top of the screen the last survey line name and the last station are displayed. Default name for the new line is given based on the Line Increment parameter. The default Start Station, direction of the Station Increment, and Direction are determined based on Sequence selection. All these parameters can be overwritten by the user as described in the Survey Setup menu description (section 9.2).

After selection is updated, it can be accepted by pressing the function key **F1**. The display returns to the Log Data screen with new settings for the new survey line.

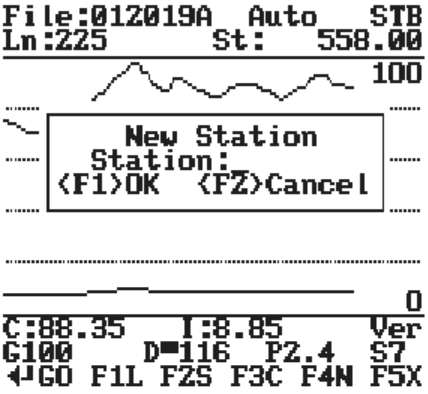
Pressing key **F2** or **<Esc>** will disregard any New Line menu changes and the program will return to the Log Data screen and measurements can be continued.

F2 (New Station)

This option is labeled **NStn** in the Text display mode, and **S** in the Graphic display mode. The New Station menus in two display modes, in the text mode (on the left) and in the graphic mode (on the right) are given below.

Selecting this option allows the operator to enter a new station number. In the Text mode Start Station and Current Stations are displayed at the top of the screen. In the Graphic mode only the Current Station is displayed. The New Station can be entered in the similar way as editing parameters in Survey Setup menu, and in the provided message box in the Graphic display mode.

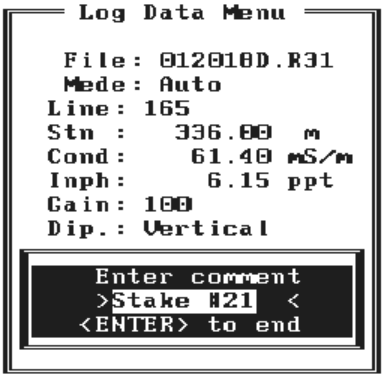
After the New Station is entered, it can be accepted by pressing the function key **F1**. The display return to the Log Data screen with new station..

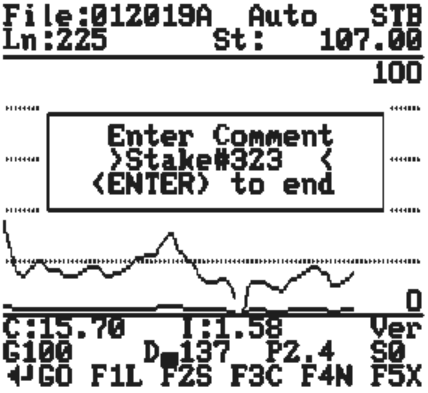


Pressing key **F2** or <**Esc**> will disregard new entry and the program will return to the Log Data screen and measurements can be continued.

F3 (Comment)

This option is labeled **Cmnt** in the Text display mode, and **C** in the Graphic display mode. Menus containing Enter Comment box in the text mode (on the left) and in the graphic mode (on the right) are given below.



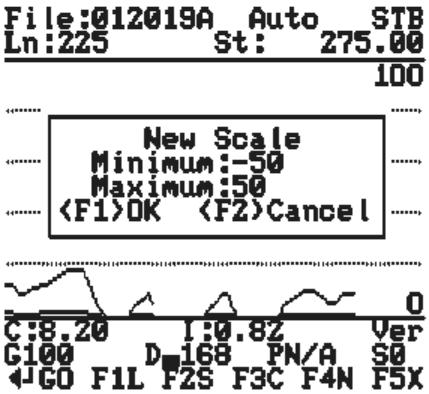


Selecting this option allows the operator to enter a comment at any point of the survey. A maximum of 11 characters can be entered as a comment. Text of the comment is saved in the file with a corresponding time stamp.

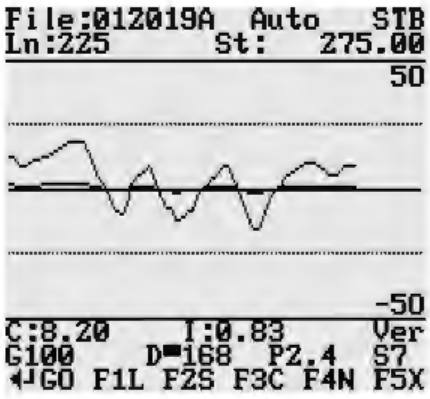
The user must exit the comment mode by pressing <**ENTER**> key.

F4 (New Scale) *only graphic display*

This option is available only in the Graphic display mode and it is labeled **N**. The Log Data screen with the entry box for New Scale parameters is given below.

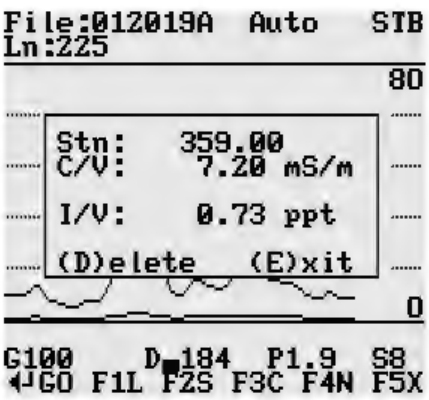


Selecting this option allows the operator to enter new scale parameters for the amplitude display. After minimum and maximum values are specified, the function key **F1** (OK) will accept new values and the display will be redrawn (see below). When the key **F2** (Cancel) is pressed the new entry is cancelled.



<**Del**>(delete reading)

This option is labeled **Rdg** in both display modes. The Delete Reading box that appears on the screen, in the text mode (on the left) and in the graphic mode (on the right) is shown below.



This function allows operator to delete previously recorded reading(s). The reading (station) to be deleted is displayed on the screen. The data will only be deleted when the key **D** is pressed. The program will then display the next previous station, and allow it to be deleted in a similar fashion. If there is no further data available, the program will provide related information.

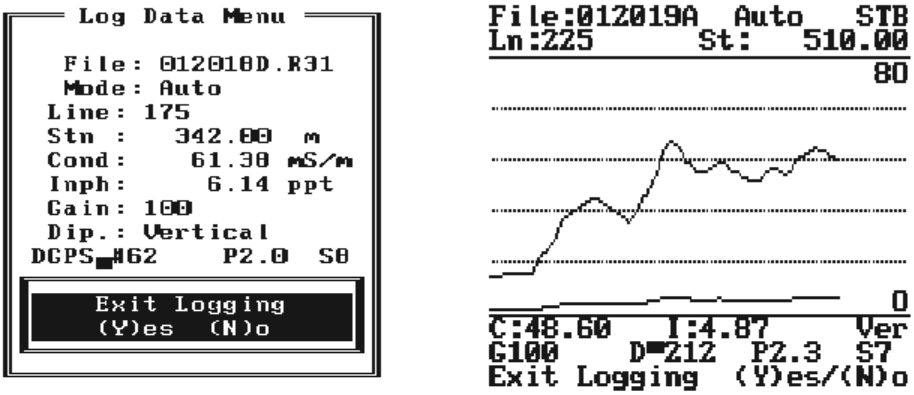
To exit delete reading mode press key **E**.

F5 (exit LOG DATA mode)

This option is labeled **Exit** in the text display mode, and **X** in the graphic display mode. After key **F5** is pressed a confirmation prompt **Exit Logging Y(es)/N(o)** will appear on the screen as shown below.

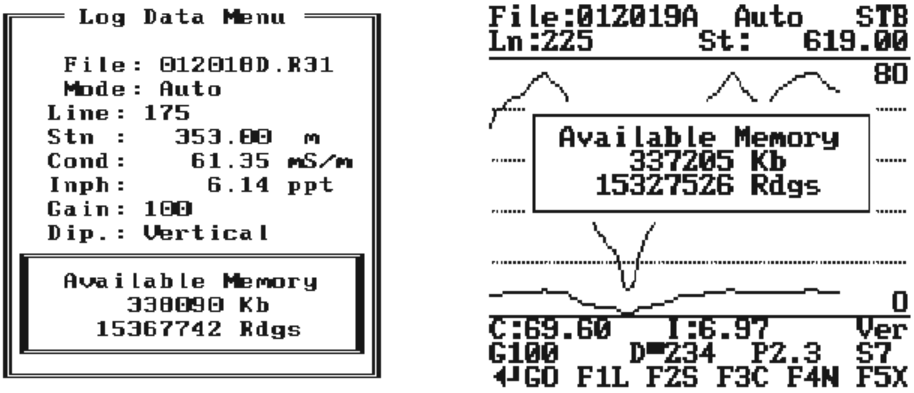
When the key **Y** is pressed the data file is closed and the program returns to the Acquiring Data menu. In order to continue survey a new data file must be created.

If the key **N** is pressed the program returns to current logging mode.



M or V (memory check, no prompt on the screen)

This label corresponding to this option is not shown on the screen. After key **M** or **V** is pressed a small window that shows the amount of available memory for data is displayed. The amount of available memory is given in Kbytes and in number of EM31 readings (one EM31 record is 22 bytes long). If GPS data is taken concurrently, one GPS record is equal to 5 or 6 EM31 readings (110 or 132 bytes).

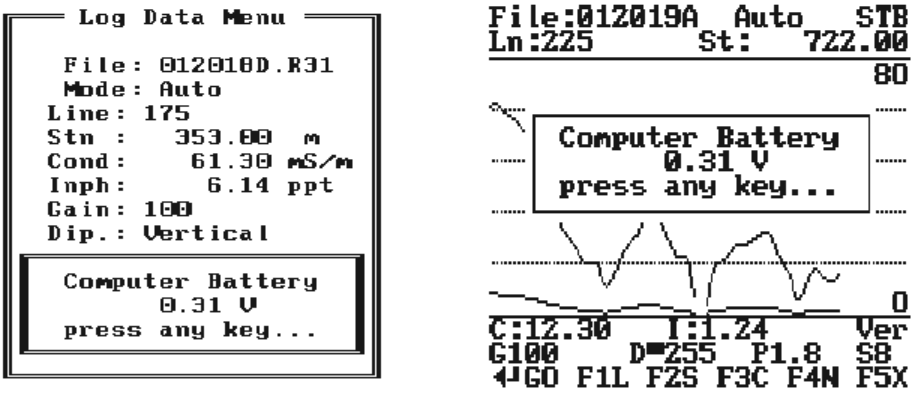


Available memory is also checked automatically during data collection. In cases where the amount of available memory in the logger is less than 10 Kbytes, the program will stop, data file will close, and a proper message will be displayed.

B (Pro4000 battery check, no prompt on the screen)

The label corresponding to this option is not shown on the screen. After key **B** is pressed a small window that shows the voltage of Pro4000 battery (in Volts) is displayed. If other than Pro4000 or Allegro field computer is used the displayed value may not be accurate.

The Pro4000 system will also warn the user when battery voltage is too low.



10. Data Transfer (Upload Files)

This chapter describes the transfer of data files from a field computer Pro4000 to PC computer using **Download EM31pro Files** option of the DAT31W program. Data files can be downloaded by alternative utilities (e.g. ProShell, Lynx, or FileScout in Allegro Field PC) and then these files can be converted to DAT31 format using option **Convert|EM31pro Files** in the DAT31W menu.

10.1 Data File Formats

Data files in the field computer are formatted in proprietary EM31pro format. The EM31pro data is saved in one data file with the extension name R31.

Files in the logger format are converted to the DAT31 format during the downloading of data. These new files have same base name with an added extension name G31. Files in the DAT31 format can be loaded and processed by the DAT31W program.

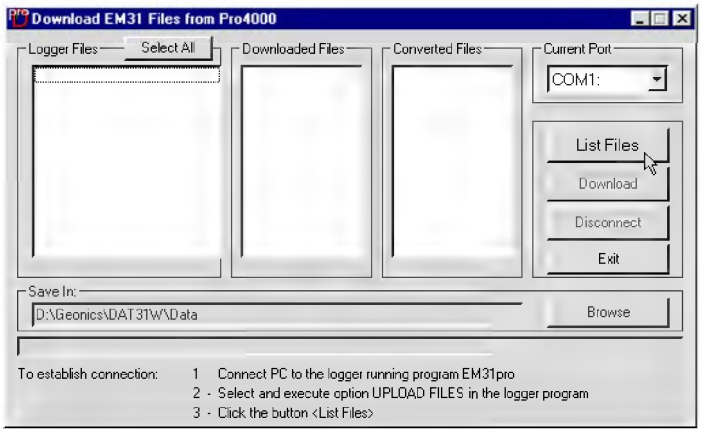
While only the DAT31 format is used in data processing, it is strongly advised that data in the raw (EM31pro) format be saved as well. In the case of any hardware malfunction, i.e. a damaged instrument cable, only the file in logger format may indicate the source of the problem. Additionally, raw data files also contain useful information about the instrument settings used during field work. Files in the EM31pro format can be converted to the DAT31 format at any time using the Convert EM31pro Files option of the DAT31W menu.

Description and sample of the EM31 files in the EM31pro format, as well as an example of a file converted to the DAT31 format are placed in Appendix A of DAT31W manual.

10.2 Upload Files Procedure

To start downloading files from the field computer, select the **Data Transfer** item in the program menu and then click on **Download EM31pro Files** from the menu item

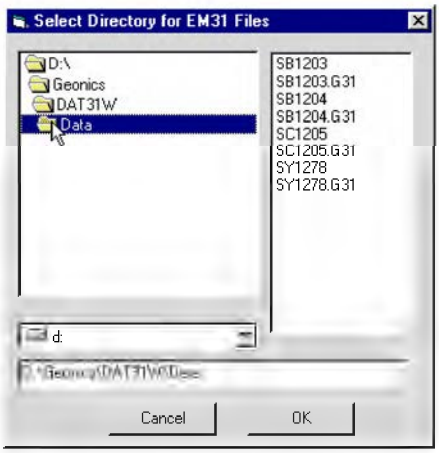
After you click the **Download EM31pro Files** item, the Download EM31 Files from Pro4000 window will appear.



The Download window has three list boxes. The first from the left, labeled Logger Files will contain, after the **List Files** button is clicked, a list of data files located in the field computer and available to download. File names, with their size in bytes will be displayed as well. The second list box,

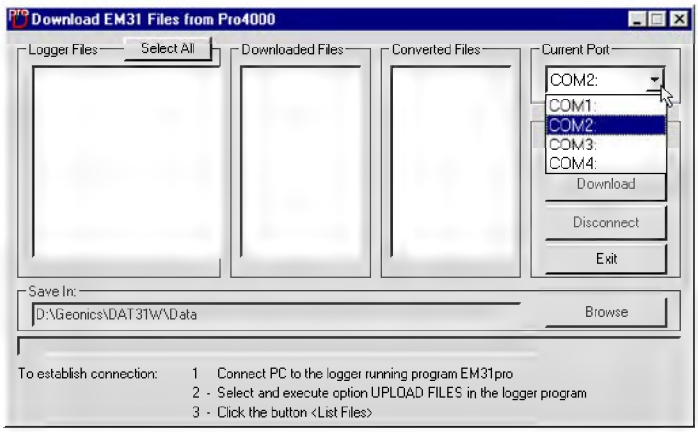
labeled Downloaded Files, will list downloaded data files in the EM31pro format, and the third, Converted Files, will list files converted to DAT31 format. If a file name already exists on the computer hard disk, an underscore followed by a letter will be added to the base name. (ie. file name ABC.R31 would be changed to ABC_1.R31, ABC_2.R31, and so on.)

To select the directory where transferred files will be placed click the **Browse** button. The Select Directory for EM31 Files window will be displayed (Figure below).



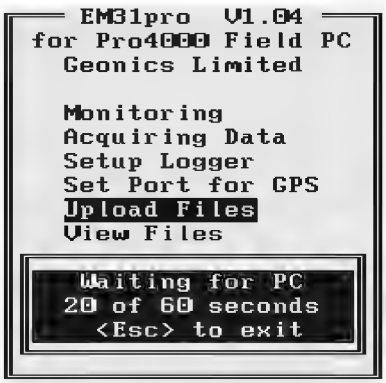
After the directory is selected, it will be displayed in the text box labelled **Save In** at bottom part of the Download EM31pro Files from Pro4000 window. The selected directory will be saved and it will be used as the default directory during subsequent DAT31W executions. If this directory is removed the C:\ directory will be used instead.

Change of the port assignment can be done by clicking the Down arrow button in the field labeled Current Port. The pull down list box will be displayed, as shown in Figure below. Select required COM port number.

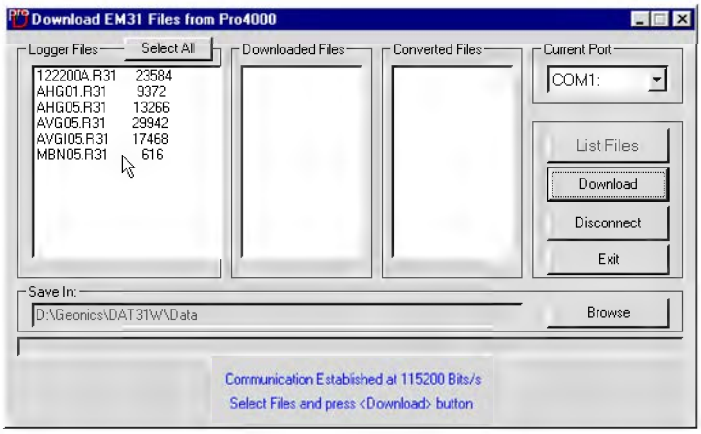


To start downloading the data files, connect the field computer (Pro4000) and PC computer with the serial cable.

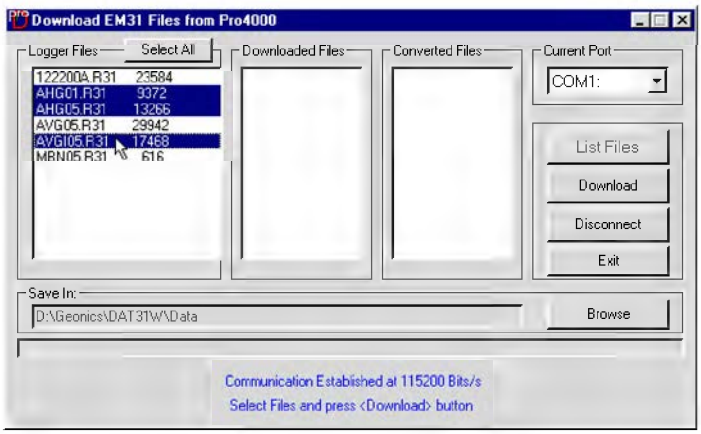
Run the EM31pro program in the logger. In the Main menu of the program select **Upload Files** option, and press <**ENTER**>. The logger screen will display the message "**Waiting for PC**" (shown in Figure below) for up to 1 minute (if time elapses repeat the procedure). On the computer click the **List Files** button in the Download EM31pro Files from Pro4000 window. At that time both programs (EM31pro and DAT31W) will establish and test the communication at the highest



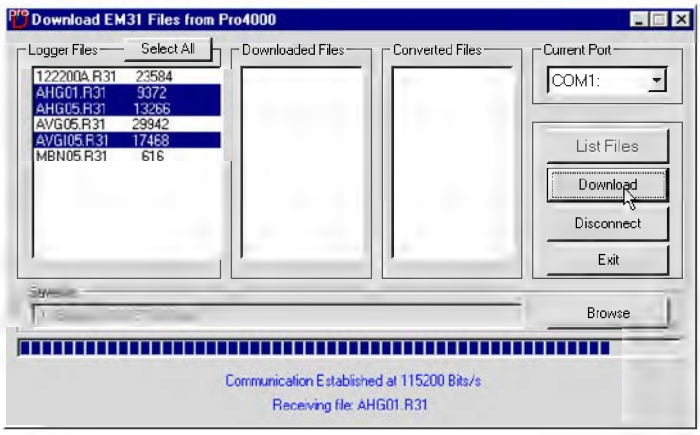
possible speed of data transfer. After several seconds the Logger Files list box will be updated with the names and sizes of data files available for download (see Figure below). At the same time, the **Download** and **Disconnect** buttons will be activated, and the **List Files** button will be deactivated.



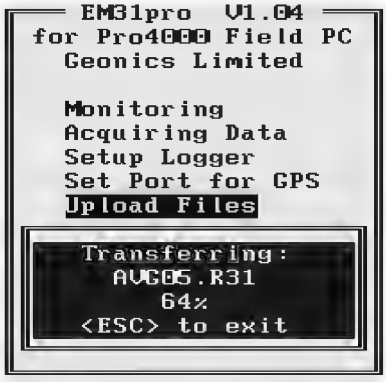
Select the files to be downloaded from the logger by clicking on individual file names in the list box (Figure below) or click the **Select All** button to select all available files. When all files are selected the **Select All** button will change to the **Unselect All** button.



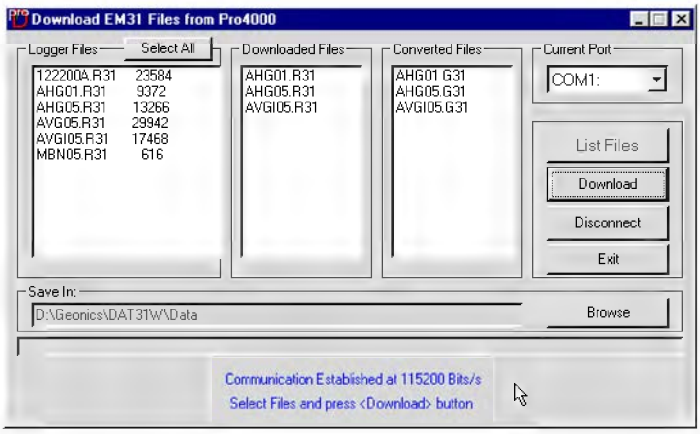
When file selection is complete click the **Download** button. The name of each transferred file is displayed at the bottom of the window as it transfers and a progress bar indicates the percentage completed, as shown in the following Figure.



At the same time the logger screen displays transmitted file name and percentage of completed uploading (Figure below). The transfer procedure can be stopped at any time by pressing <**Esc**> key on the logger keypad.



Transferred files (in EM31pro format) will be displayed in the centre list box. After the transfer of all selected files is complete, files in the EM31pro format are automatically converted to the DAT31 format (with extension name G31). Converted files will be displayed in the Converted Files list box (see Figure below). Converted files (with extension name G31) can be loaded and processed further in the program.



Click the **Disconnect** button to cancel communication with logger. The Download EM31 Files from Pro4000 window will remain on the screen and next data transfer session (i.e. from another logger) can be performed. Clicking the **Exit** button will stop Data Transfer function and the Download EM31 Files from Pro4000 window will disappear.

11. View Files

This option allows to view recorded data files. After the View Files option is selected in the Main Menu the View Files menu with a list of data files and their size appears on the screen. This menu is presented below.

Select the file by using **Down** and **Up** arrow keys. When the desired file is highlighted press function key **F1** to view contents of this file. Pressing key **F2** will return the program to the EM31pro Main menu.

After key **F1** is pressed the View File menu with readings taken at the first station of the first survey line in the file is displayed, as shown below.

At the top of the screen name of the data file and the EM31 mode are displayed. Then the Line Name, Station, and readings with the instrument dipole mode (V for Vertical or H for Horizontal) are shown. The survey line direction (Dir) and the fiducial marker (Mkr) presence **Y**(es) or **N**(o) are displayed as well. If the file contains comments, the text will be displayed between neighbouring stations.

The **Right** arrow key is used to show next station (NextStn) and the **Left** arrow key will move display to previous station (PrevStn) readings. Survey lines can be changed by pressing **Down** and **Up** arrow keys. The **Down** arrow key will switch the display to the first station of the next survey line (NextL), and the **Up** arrow key will show the first station readings of the previous survey line (PrevL). If the last or first station of a survey line will be reached, or the last survey line in the file will be encountered, the program will provide appropriate information.

12. Delete Files

This option allows you to delete data files from the field computer memory. After the Delete Files option is selected in the Main Menu the Delete Files menu with a list of data files and their size appears on the screen. This menu is presented below.

Select the file by using **Down** and **Up** arrow keys. When the file to be deleted is highlighted press function key **F1** to delete the file. Pressing key **F2** will return the program to the EM31pro Main Menu.

After key **F1** is pressed a confirmation prompt appears on the screen, as shown below.

If key **Y** will be pressed the file will be permanently deleted from the field computer memory. When key **N** is pressed the confirmation prompt disappears and display shows the list of available data files.

Exit the Delete Files menu by pressing the function key **F2**. The program will return to the EM31pro Main Menu.

13. End Program

To end the program highlight the Exit option in the Main Menu and press the <**ENTER**> key. The program will stop, and it will return to the DOS prompt.

Appendix A

A.1 Using the EM31pro with a GPS System

The EM31pro program accepts input from GPS systems that stream NMEA-0183 compatible data. through their output port. The program uses two NMEA messages: GGA and GSA. The entire GGA message is written to the EM31pro data file, while the GSA message is used only to display PDOP index on the logger screen.

The GPS system means (control device, receiver panel, or manufacturer software) must be used to set GPS receiver communication parameters, to specify frequency of GPS output, and number and type of NMEA messages sent by the GPS system output port. Any GPS system can send various NMEA messages. **It is important to select only two messages (GGA and GSA) that are actually used by EM31pro.** The program will accept any GPS string sent by the GPS receiver, however it uses time to process GPS data that is not being used. Therefore, selecting a larger number of NMEA messages for GPS output will result in slower data acquisition of EM31pro. Normally, the EM31pro running in Pro4000 logger uses less than 100 ms to process and record GPS data from two NMEA messages, GGA and GSA.

Only message GGA is necessary to position EM31 data. If message GSA is not available in a particular system, the EM31pro will function and record position data based on GGA message. Lack of GSA message will result in PDOP index displayed as Not Available (N/A) on the logger display.

The EM31pro dedicates one line of the display to show GPS status. A label **DGPS** (Differential Global Positioning System) in text mode or **D** in graphic mode indicates that GPS readings are differentially corrected in real time Label **AGPS** (Autonomous Global Positioning System) or **A** in graphic mode indicates lack of differential correction. On the right side of **DGPS** or **AGPS** (**D** or **A** in graphic mode) a label small square is displayed. This square should move down and up with the frequency of GPS update rate (usually 1 second intervals). If the square is not moving for longer period of time it means that GPS system is not working or that it is not connected to the field computer. Number of recorded GPS positions are displayed on the right side of the small square. This number is updated only in the logging mode, when the data are recorded. (In Stand By mode or during Monitoring only the moving square, and updated values of PDOP and number of tracked satellites, indicate presence of GPS input).

Two more GPS parameters are displayed on the logger screen. These are index PDOP shown by label **P** and number of tracked satellites represented by label **S**. The index called PDOP (Position Dilution of Precision) measures the strength of satellite coverage for a given area. PDOP is affected by the number of satellites visible and their relative positions in the sky. The smaller the number of PDOP the stronger the satellite coverage is. When there are more than 5 satellites widely spaced visible, the PDOP is 4 or less. However, when there are less satellites visible, or they are unevenly spaced in the sky, PDOP values can be 6 or higher. In most cases, the PDOP in an open sky is less than 3, and most accuracies given for many GPS systems are given for this norm. Refer to GPS documentation and literature for more information related to error sources of GPS positioning.

A.2 Description of GGA and GSA Data Messages

GGA Data Message

The GGA message contains the GPS position information and it is the most widely used NMEA data message. This message takes the following form:

$GPGGA,hhmmss.ss,ddmm.mmmmm,s,dddmm.mmmmm,s,n,qq,pp.p,saaaaa.aa,u, +xxxx.x,M,sss,aaaa*cc<CR><LF>

Definition of GGA message component:

hhmmss.ss	UTC time in hours, minutes, seconds of the GPS position
ddmm.mmmmm	Latitude in degrees, minutes, and decimal minutes
s	s=N or s=S, for North and South latitude
dddmm.mmmmm	Longitude in degrees, minutes, and decimal minutes
s	s=E or s=W, for East and West longitude
n	Quality indicator, 0 = no position, 1 = raw, no differentially corrected position, 2 = differentially corrected position, 9 = position computed using almanac information
qq	Number of satellites used in position computation
pp.p	HDOP = 0.0 to 99.9
saaaaa.aa	Antenna altitude
u	Altitude units, M=meters
+xxxx.x	Geoidal separation (requires geoidal height option)
M	Geoidal separation units, M = meters
sss	Age of differential corrections in seconds
aaaa	Base station identification
***cc**	Checksum
<CR><LF>	Carriage return and Line feed

GSA Data Message

The GSA message contains active satellites and PDOP value. The GSA message is given in the following form:

$GPGSA,c1,d1,d2,d3,d4,d5,d6,d7,d8,d9,d10,d11,d12,d13,f1,f2,f3*cc<CR><LF>

Definition of GSA message components:

c1	Mode, M = manual, A = automatic
d1	Mode, 2 = 2D, 3 = 3D
d2-d13	Satellites used in position computation (range 0 to 32)
f1	PDOP (range 0 to 99.9)
f2	HDOP (range 0 to 99.9)
f3	VDOP (range 0 to 99.9)
***cc**	Checksum
<CR><LF>	Carriage return and Line Feed

Appendix B

B.1 Description of Data File in EM31pro Format

Each record contains 22 characters, including line feed at the end of each record.

Header of the file (contains two records starting with characters E and H)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
E	M	3	1	M	K	2		V	1	2	3	Survey Type			UT	ID	IM	IC			10
H		File Name										Time/Wheel/Samples									10

EM31MK2	-	identification of program file (EM31SH for short EM31)
V123	-	version number (V1.23)
Survey Type	-	GPS (if GPS Input Enabled) or GRD (grid)
UT	-	unit type (0 = meters, 1 = feet)
ID	-	EM31 Dipole Mode (0 = Vertical, 1 = Horizontal, 2 = Both)
IM	-	EM31 survey mode (0 = Auto, 1 = Wheel, and 2 = Manual)
IC	-	EM31 component (0 = Both, 1 = Inphase)
File Name	-	file name, maximum 8 characters
Time/Wheel/Samples	-	this field depends on EM31 survey mode Auto Mode -Time Increment in seconds Wheel Mode - Wheel Increment (user units, see IT) Manual Mode - Samples/Reading
10	-	Line Feed character

Header at the start of survey line (contains four records starting with L, B, A, and Z)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
L	Line Name - 8 characters																				10
B	Start Station (Format F11.2)																				10
A	Dir							Increment (Format F11.2)													10
Z	D	D	M	M	Y	Y	Y	Y		H	H	:	M	M	:	S	S	.	s	s	10

Line Name	-	Line Name, maximum 8 characters
Start Station	-	Start Station for the Line, format F11.2
Dir	-	Direction of the Line (E, W, N, or S)
Station Inc.	-	Station Increment, format F11.3
Date	-	Date when Line was created, format DD-MM-YYYY
Time	-	Real Time when Line was created, format HH:MM:SS.ss
10	-	Line Feed character

Reading

1	2	3 4 5 6 7	8	9 10 11 12	13	14 15 16 17 18 19 20 21	22
I	Gn	Reading1		Reading2		Time Stamp (HHMMSSss)	10

I - indicator T, or 2
- **T** - First reading at the station (default for Auto mode)
- **2** - second reading at station (possibble only in Manual mode)

Gn - information byte, one character parameter,
the ASCII number of this character indicates following:

Bit	Decimal	Value and Meaning		
7	128	1		*not used*
6	64	Marker	= 1	*trigger pressed*
			= 0	*otherwise*
5	32	Mode	= 1	*Vertical*
			= 0	*Horizontal*
4	16	0		*not used*
3	8	0		*not used*
2	4	Range 3		
1	2	Range 2		
0	1	0		not used

Range 3 and Range 2 represent sensitivity (gain) as follows

Both components (OPER mode)

Sensitivity	Range 2	Range 3	Multiplication Factors	
1000	1	1	Conductivity	-0.25
100	0	1	Conductivity	-0.025
10	1	0	Conductivity	-0.0025

Multiplication factor for Inphase is the same for all ranges: -0.025

Inphase component (COMP mode)

Sensitivity	Range 2	Range 3	Multiplication Factors	
1000	1	1	Inphase	-0.0625
100	0	1	Inphase	-0.00625
10	1	0	Inphase	-0.000625

Conductivity is not recorded in COMP mode.

Multiply Reading by above factors to obtain reasult in mS/m or ppt.
If short EM31 is used divide all Inphase data by 3.35.

Reading1 - five character field containing instrument output.
Conductivity if Both components, Inphase if Inphase was selected.
includes sign (+ or -) and four digits

Reading2 - five character field containing instrument output.
Inphase if Both components, not used if Inphase was selected.
includes sign (+ or -) and four digits

Time - time stamp of the reading in the 24 hour clock format HHMMSSss which corresponds to HH:MM:SS.ss (hours, minutes, seconds and hundreth of second).

10 - Line Feed character

Comment

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
C	Comment (maximum 11 characters)												Time Stamp (HHMMSSss)								10

New Station

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
S	New Station (Format 11.2)												Time Stamp (HHMMSSss)								10

Deleted Records

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
X	Gn	Reading											Time Stamp (HHMMSSss)								10
X	Comment (maximum 11 characters)												Time Stamp (HHMMSSss)								10

GPS Data Message Records

Each GPS record (GGA Message) is broken in to several 20 characters strings and placed in the EM31pro data file which contains 22 characters records, including one character indicator and line feed at the end of each record. The GPS sequence starts at the line which contains character **@** as the first character, then records that contain continuation of the same message start with character **#**. The GPS sequence ends with a line starting with the character **!**. The last line contains logger time stamp in milliseconds for given GPS reading. A sample of the GPS message written in EM38pro format is given below.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
@	$	G	P	G	G	A	,	h	h	m	m	s	s	.	s	s	,	d	d	m	10
#	m	.	m	m	m	m	m	,	s	,	d	d	d	m	m	.	m	m	m	m	10
#	m	,	s	,	n	,	q	q	,	p	p	.	p	,	s	a	a	a	a	a	10
#	.	a	a	,	u	,	+	x	x	x	x	.	x	,	M	,	s	s	s	,	10
#	a	a	a	*	c	c	CR	LF													10
!													H	H	M	M	S	S	h	h	10

The GPS sequence may contain 5 or 6 records. Component of the GGA message may differ in length, however they are placed in the same number of columns. Refer to Appendix A (section A.2) for definition of each component of GGA data message.

B.2 Example of Data File in EM31pro Format

The EM31pro data file records are written in binary format, therefore the file may have different shape when displayed or printed, depending on particular video or printer settings.

```
EM31MK2 V104GPS0000
H 122200A    0.200
L500
B       0.00
AW            1.000
Z12222001 00:12:21.58
T¤-0648-0652 00150419
T¤-0652-0656 00150441
T¤-0866-0875 00150462
T¤-0884-0888 00150484
T¤-0990-1002 00150501
@$GPGGA,050745.00,433
#6.59295,N,07936.6514
#5,W,2,7,1,140.81,M,-
#35,M,5,118*5A
!            00150515
T¤-1012-1011 00150521
T¤-0878-0873 00150540
T¤-0780-0784 00150560
T¤-0918-0929 00150580
T¤-1041-1053 00150599
@$GPGGA,050746.00,433
#6.59298,N,07936.6514
#7,W,2,7,1,141.19,M,-
#35,M,4,118*57
!            00150608
T¤-1101-1113 00150622
T¤-1284-1294 00150640
T¤-1620-1643 00150660
T¤-1814-1844 00150680
T¤-2149-2160 00150702
@$GPGGA,050747.00,433
#6.59299,N,07936.6515
#0,W,2,7,1,141.19,M,-
#35,M,5,118*50
!            00150717
T¤-2179-2180 00150725
T¤-1646-1640 00150745
T¤-1511-1507 00150763
T¤-1465-1468 00150783
T¤-1429-1433 00150810
@$GPGGA,050748.00,433
#6.59301,N,07936.6515
#0,W,2,7,1,141.13,M,-
#35,M,6,118*56
!            00150815
T¤-1420-1424 00150820
T¤-1753-1767 00150841
T¤-1897-1909 00150862
T¤-2020-2029 00150881
T¤-2166-2178 00150904
@$GPGGA,050749.00,433
#6.59303,N,07936.6514
#5,W,2,7,1,140.89,M,-
#35,M,5,118*50
!            00150914
```

Appendix C

C.1 Performing Hard Reset in Allegro and Pro4000

To perform hard reset in Allegro or Pro4000 hold down the ON/OFF key for 8 to 10 seconds. Release the key when the reboot process begins.

C.2 Panning the Display in Allegro and Pro4000

If the display in Allegro or Pro4000 is shifted at the beginning of the program you can do following:

You can move the display window by pressing the GOLD key plus the desired arrow key in Allegro, while in Pro4000 the display window can be moved by pressing the GREEN key plus the desired arrow key.

C.3 Operating DOS in Allegro

To start DOS (if the Allegro operates under control of Windows CE), tap the **Start** button on the Windows CE Desktop and select **Programs**|**Boot to DOS**. In DOS you can operate the Allegro by using standard DOS commands from the DOS prompt or through FileScout, a DOS File Management Utility.

C.4 Short Overview of Programs FileScout/ProShell and Lynx

Two programs, FileScout and Lynx, are supplied with the Allegro system and can be used to transfer files between the Allegro and a desktop Windows based computer. Programs ProShell (similar to FileScout) and Lynx are supplied with the Pro4000 system.

To run FileScout in Allegro, type **FS** at the DOS prompt and then press <ENTER>. To run ProShell in Pro4000, type **PS** at the DOS prompt and press <ENTER>. Use the function keys and arrow keys to make selections in both, FileScout and ProShell.

The program ProLink which is used to transfer files between Allegro or Pro4000 is factory installed in the Allegro/Pro4000 ROM (drive A:). When FileScout or ProShell is run ProLink is automatically initiated.

Lynx runs on computers equipped with Windows 95 or higher. To install Lynx from Allegro disk insert CD disk follow the instructions given by the install programs. To install Lynx from Pro4000 disks, insert the Pro4000 Setup disk (Utility disk #1) into drive A: on your computer and run the Setup program. The Lynx icon will appear on your desktop after installation is complete. When Lynx is started two Windows Explorer type screens will be displayed. The top screen, labeled Local, displays the contents of the PC. The bottom screen, labeled Remote, displays the contents of the Allegro or Pro4000 assuming a connection is established. Several file management functions can be performed using Lynx, including File Transfer, renaming folders, creating new folders or sub-folders, and deleting files.

C.5 File Transfer Using Lynx

Establishing Communication

To transfer data to and from a base computer, attach the cable (null modem serial communication cable) between the Allegro (or Pro4000) and the computer COM ports. Run FileScout on the Allegro (type command **FS** to run FileScout) or ProShell on the Pro4000 (type command **PS** to run ProShell) and Lynx on the PC computer.

Correct communication ports must be selected on both computers. To set up the serial port on the PC, from Lynx select the **Transfer/Select COM Port** menu option. To set up the communication port on the Allegro/Pro4000, press <F5>(Xfer) from main screen of FileScout or ProShell, and then press <F1> to toggle between ports COM1 and COM2.

Juniper Systems recommends that the Allegro (or Pro4000) is in auto baud rate detection mode (the default setting). In this mode, the Allegro (or Pro4000) tries to establish communication at 115K baud, and in case communication fails at this rate, it automatically steps down to the next slowest rate until communication is established.

To start communication click on the **Connect** button (the green circulating arrows in the centre tool bar) or select the Transfer/Connect to Remote menu option from Lynx. When connection is established the contents of the Allegro (or Pro4000) Field Computer will be displayed in the Lynx bottom Remote view screen.

Transferring Files to the Allegro from the PC

Select the folder in the Remote view screen. Transferred files will be saved in this folder.

In the Local view screen select files to be transferred to the Allegro (or Pro4000).

Click the Down arrow button or select Transfer/Send to Remote from the main menu. File transfer starts immediately. In cases where the selected file exists in the logger the program will prompt for permission to overwrite.

Transferring Files from the Allegro to the PC

Select the folder in the Local view screen. Transferred files will be saved in this folder.

In the Remote view screen select files to be transferred to the PC.

Click the Up arrow button or select Transfer/Receive from Remote from the main menu. File transfer starts immediately. If selected files exist in the selected folder in the PC the program will prompt for permission to overwrite.

When the transferring session is finished click the Disconnect button before disconnecting the serial cable. Otherwise, the Esc key must be pressed on the logger to return the Allegro (or Pro4000) to normal function.

Please refer to Allegro or Pro4000 Field Computer User's Manual (Section 5) for more detailed description of FileScout/ProShell and Lynx functions.

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EM 61-MK2
and
EM61-MK2HP

4 CHANNEL HIGH SENSITIVITY METAL DETECTORS

OPERATING MANUAL

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July 2005

EM6I-MK2
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4 CHANNEL HIGH SENSITIVITY METAL DETECTORS
OPERATING MANUAL

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EM6I-MK2 HIGH SENSITIVITY METAL DETECTOR
OPERATING INSTRUCTIONS

INTRODUCTION

The **Geonics** EM6I-MK2 is a high sensitivity high resolution 4 channel time-domain metal detector which is used to detect both ferrous and non-ferrous metalic objects. It consists of a powerful transmitter that generates a pulsed primary magnetic field, which induces eddy currents in nearby metallic objects. The decay of these currents is measured by two receiver coils mounted on the coil assembly. The responses are recorded and displayed by an integrated computer based digital data logger with real time numerical and graphic display. Two ports on the logger allows simultaneous collection of EM and GPS data. For further processing and interpretation data can be transferred to the PC type of computer.

The EM6I-MK2 detects a single 200 litre (55 gallon) drum at a depth of over 3 meters beneath the instrument, yet it is relatively insensitive to interference from nearby surface metal such as fences, buildings, cars, etc. By making the measurement at a relatively long time after termination of the primary pulse, the response is practically independent of the electrical conductivity of the ground.

Due to its unique coil arrangements, the response curve is a single well defined positive peak, greatly facilitating quick and accurate location of the target, the depth of which can usually be estimated from the width of the response and/or from relative response from each of the two receiver coils.

A single operator can carry the EM61-MK2 antenna system from a belt harness, in which case the data logger is usually set to record the data at fixed increments of time (with the facility to add fiducial records when passing by known locations). Alternatively, the operator can pull the system on an optional trailer, in which case an odometer mounted on the axle of the trailer wheel automatically triggers the data logger to record the measurements.

An optional set of small sensors provides for a hand-held operation of the system, for high mobility and increased sensitivity to small near surface objests.

Integrated control switch allows for synchronous operation of multiple units if desired.

With its comprehensive detection, depth of investigation and speed of surveying, the EM61-MK2 is an ideal metal-detector. The ease and certainty with which survey results can be interpreted make the EM61-MK2 practical for both the occasional user and expert geophysicist.

A. EM6I-MK2 SYSTEM

1. System Assembly

The EM6I-MK2 consists of three major parts: coil assembly, backpack with battery and processing electronics console and digital data recorder.

Figure 1 shows the system assembled for the trailer mode of operation.

To assemble the trailer set the bottom coil (larger of the two) on the ground with the top of the coil facing the ground and slide the wheel assembly into the wheel guide on the side of the coil so that the wheels are outside the coil frame. Make sure that the wheel assembly with the short cable (1) is placed on the right side of the coil as indicated on the Figure 1. Secure the wheels with the latch. Rotate the coil so that the main coil frame is resting on the wheels. Set the four stand off bars to each corner of the bottom coil and lock it with wing nuts.

Assemble the second (smaller) coil frame as indicated on the Figure 1, and lock it to the coil stand off.
a) For instrument with the boom: attach the coil section of the boom to the main coil by aligning the self-locking key with the socket. Turn the conical knob on the end of the boom anti-clockwise so that the expansion ring collapses. Push the end of the boom through the socket and turn the knob clockwise so that the expansion ring expands and locks. To complete the assembly of the boom push the top portion of the boom (section with logger holder) into the coil section of the boom, and lock it by the clockwise rotation of the black lock nut located on the coil section of the boom. Make sure that the 4 pin lock ring is aligned so that when two sections of the boom are locked, the logger holder is facing up. Slide the logger (*PRO4000* field computer) in to the logger holder and secure it by the thumb screw located under the holder.
b) For instrument with the handle (Figure 1-A-1) set the handle (s) into the handle bracket located on the bottom coil and lock it with the attached locking pin on each side. Set the logger into the logger holder. Use appropriate hole (one of four) on the holder to obtain desired logger viewing angle. Secure the logger with the thumb screw.

Connect the wheel cable to the odometer connector on the bottom coil frame. Interconnect the bottom and top coils with the coil interconnection cable (2) cable. An optional carrying net, suspended across the top coil could be used to carry the console cables and spare battery to and from the survey site.

Set the fresh (recharged) battery into the backpack and interconnect the "REC" connector on the electronic console with the logger using logger cable (3), and connect the "COIL" connector on the console to the coil connector box located on the bottom coil using coil cable (4), as indicated on Figure 1. Place the backpack on your back and adjust the length of the straps to the most comfortable position. Connect end of the boom to the console harness for free hands operation of data logger

For a survey that does not allow a passage of 1 m width of coil assembly, set can be assembled as shown in Figure 1-B or Figure 1-B-1. For the "narrow" operation with the handle, remove handle brackets from wider side of bottom coil and set it close to the narrow side, as per Figure 1-B-1.

For an option of operation without the wheels, in case that the wheels are not available or the terrain does not permit use of wheels, use the coil assembly carrying belt with four nylon straps and attach it to the main coil frame as shown in Figure 1-C. The strap should be adjusted so that the main coil is about 40 cm from the surface of the ground when it is being carried.

Since the EM6I-MK2 is extremely sensitive even to the very small metallic objects, make sure that you do not carry any metal objects like rings, watches, knives, keys, etc., while operating the system in the **harness** mode. During the operation the logger should not be closer than 25 cm (10") from the coil assembly, otherwise the noise will be introduced.

The backpack console could be carried by the same person that carries the coil assembly, or alternatively by a second person in front of, or behind the person carrying the coil assembly. To eliminate introduction of noise, make sure that the backpack is separated at least 15 cm (6") from the coil assembly.

2. EM6I-MK2 Console

The EM6I-MK2 backpack houses electronics console with the processing electronics, and the battery pack.

The connector (bottom) side of the console front panel houses three connectors and the Master (M) / Slave (S) operation control switch. The "COIL" connector (8 sockets) provides a port for the signal from receivers and transmitter coils. The "REC" connector (10 pins) provides for interface between electronic console and the control computer (logger). The "SYNC" port in connection with the "M/S" switch provides an option for synchronous operation of two or more EM61-MK2 units. For the single unit operation, the switch should be set to (M) position. For the operation of multiple units, one (control) unit should be set to the "M" position and all other units to the "S" position. A special (optional) cable is used to interconnect all console for simultaneous operation.

The logger controls the operation of the whole system and is used as a digital data recorder. The operation of the logger is described in section B of this manual. Note that for the proper operation of the instrument, as well as the recorder, it is necessary to interconnect console with the logger by the supplied cable (3).

The small LED lamp on the topside of the console indicates if the system is turned on under control of the logger. A small speaker with its associated volume control and output for external earphone, located near the power lamp, is used as an audio monitor of the response. The push-pull circuit breaker next to the audio control is the main fuse for protecting the electronic from overload, in case of instrument malfunction. For the proper operation of the system the circuit breaker button has to be pushed in.

The mode switch on the panel allows operation of the instrument in the four channel (4) mode or in the differential (D) mode. In the four channel mode, the instrument records four time channels measured by the bottom receiver coil, while in the D mode three channels are recorded from the bottom coil and one channel from the top receiver coil. D mode provides for operation in the differential mode that is used later during processing for target depth calculation and suppression of near surface response. See Section B of this manual, for more detail about the differential mode of the operation.

Note that regardless of the mode of operation; four channel mode (4) or differential mode (D), the top coil has to be connected to the coil connector box. Also, note that when instrument operation is in D mode that the T channel of EM61-MK2 is equivalent to the T channel of EM61 (EM61-MK2 predecessor). In either mode of operation "D" or "4", the channel 3 of EM61-MK2 is equivalent to the B channel of EM61.

3. Notes on Multiple Gates Operation

Original models of EM61 have only one channel where the response is sampled at one point on the decay curve. In order to increase the capabilities of the system, the latest model (MK2) has four channels, where the response is sampled and recorded at four time positions along the decay curve.

The multiple gates allow discrimination of the targets based on the different response decay rate, that depends on the target size, shape, material and orientation. The early channel detects targets with short and long decay rates from small, medium and large targets, while the late channel detects targets with the longer time constant (larger targets) only. The apparent time constant channel, proportional to the ratio between the early and the late gate signal, that is automatically calculated during the processing, allows classification of the targets with the same or similar characteristics.

4. Hand-held Option - EM61-HH-MK2

The EM61-HH-MK2 is the hand-held mode option for the EM61-MK2 High Sensitivity Metal Detector. In this mode of operation the standard sensor set is replaced with a small set of coils. The sensors can be used either with or without wheels. In the operation without wheels the wand with the sensors is used in a sweeping mode in front of the operator. In the case of the wheel operation mode, the wand with the sensors is set into the wheel assembly that allows a more controlled inline operation.

In the case of the wheel operation the recording is initiated by the wheel odometer mounted inside the wheel assembly, or by setting the automatic time-based mode of operation. The second option, automatic, is the normal mode of operation for the recording in the non-wheel mode. The rest of the operation of the system is the same as for the standard unit. Note that the registration of targets can be either by audio mode, permanent record mode or both modes simultaneously.

4.1 Sensors Assembly - Wheel Option - Figure 2A(B)

To assemble the unit slide end of the sensor into slot **S** on the wheel assembly, align the block on the main tube with the socket on the wheel assembly and close latch L. Connect the coil cable (4A) to the coil connector on the main console.

The models that are supplied with the wheel mode, have the option of selecting 10 cm or 20 cm sampling intervals. The 20 cm recording interval is the same as on the standard EM61 unit (wheel mode), where the 10 cm sampling interval complements the higher resolution of the small sensors size of the hand-held unit. To select 10 cm or 20 cm sampling rate set the rate switch on the wheel assembly to either 01 or 02 position respectively, see Figure 2B. Note that if the 10 cm rate was selected, the

maximum surveying speed should not exceed 1 m/S , that is ½ of the maximum speed with the standard EM61-MK2 in the trailer mode.

4.2 Sensor Assembly - Non Wheel Operation - Figure 2C

For the non-wheel operation use the provided harness to carry the sensor assembly.

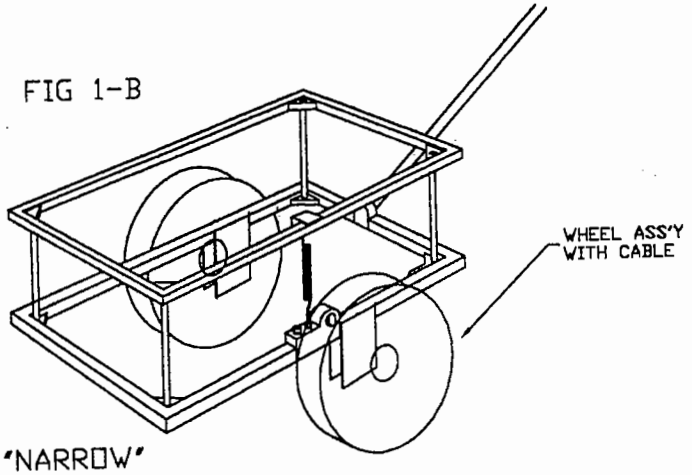
Set the boom stabilizing handle into the logger holder and lock it with the provided thumb screw.

As per Figure 2C, set the pivot bar into the backpack and adjust the strap lengths to the most comfortable configuration. Connect the coil cable to the console coil connector.

The optimum operational height of sensors is 15 to 20 cm (6" to 8") from the surface of the ground.

Continue with the operation as with the standard set of sensors.

FIG 1-B



"NARROW"

TRAILER ASS'Y

"WIDE"

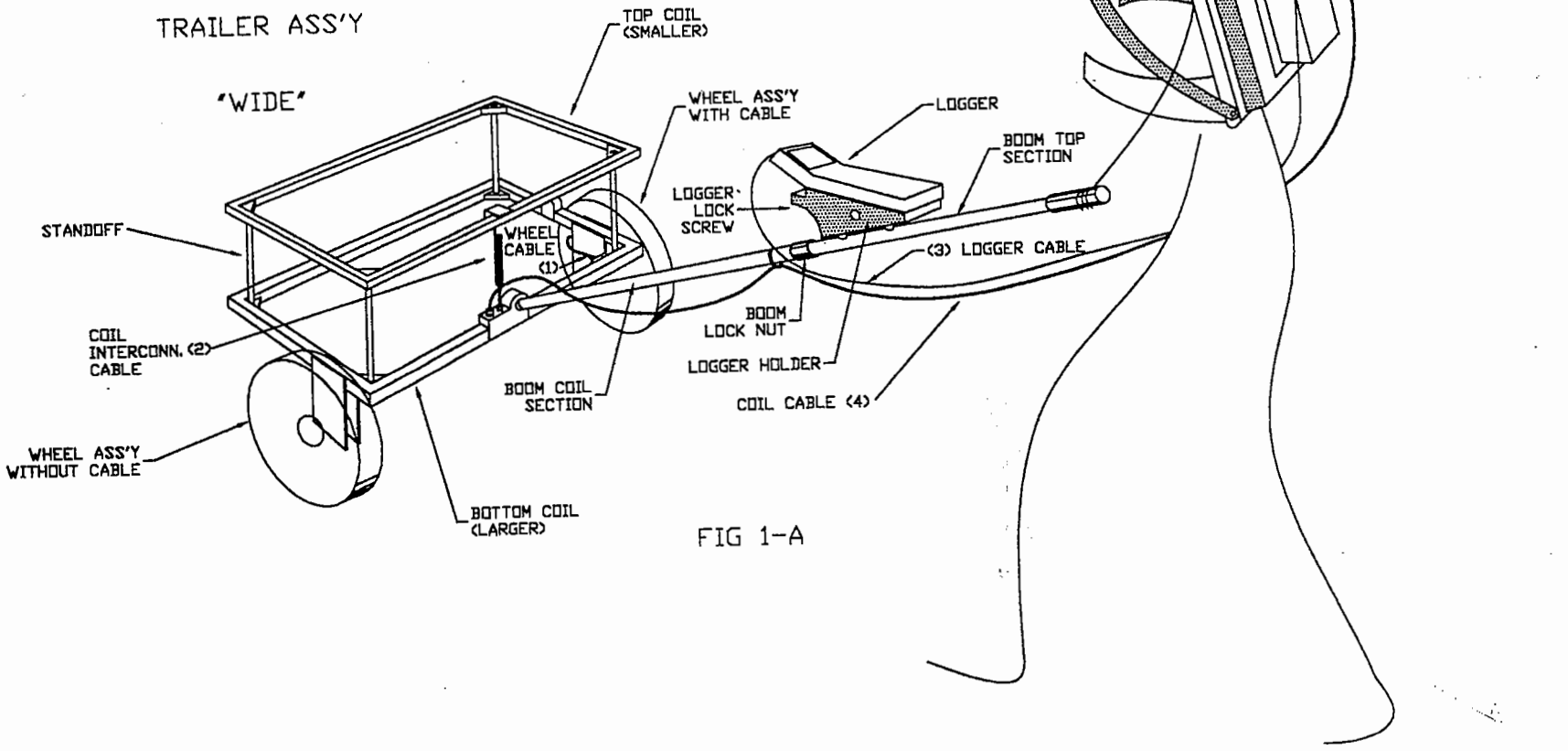
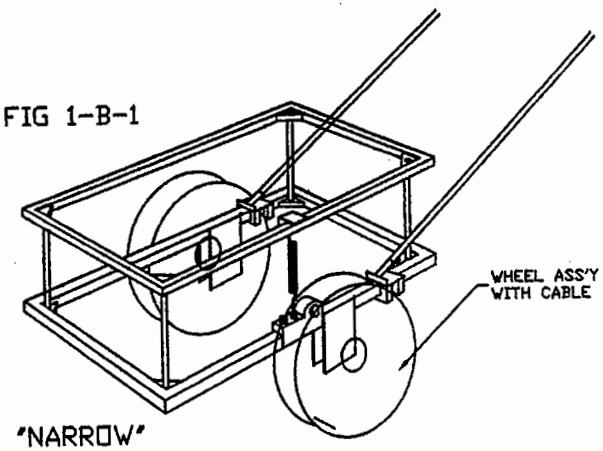


FIG 1-A

FIG 1-B-1



"NARROW"

FIG 1-A-1

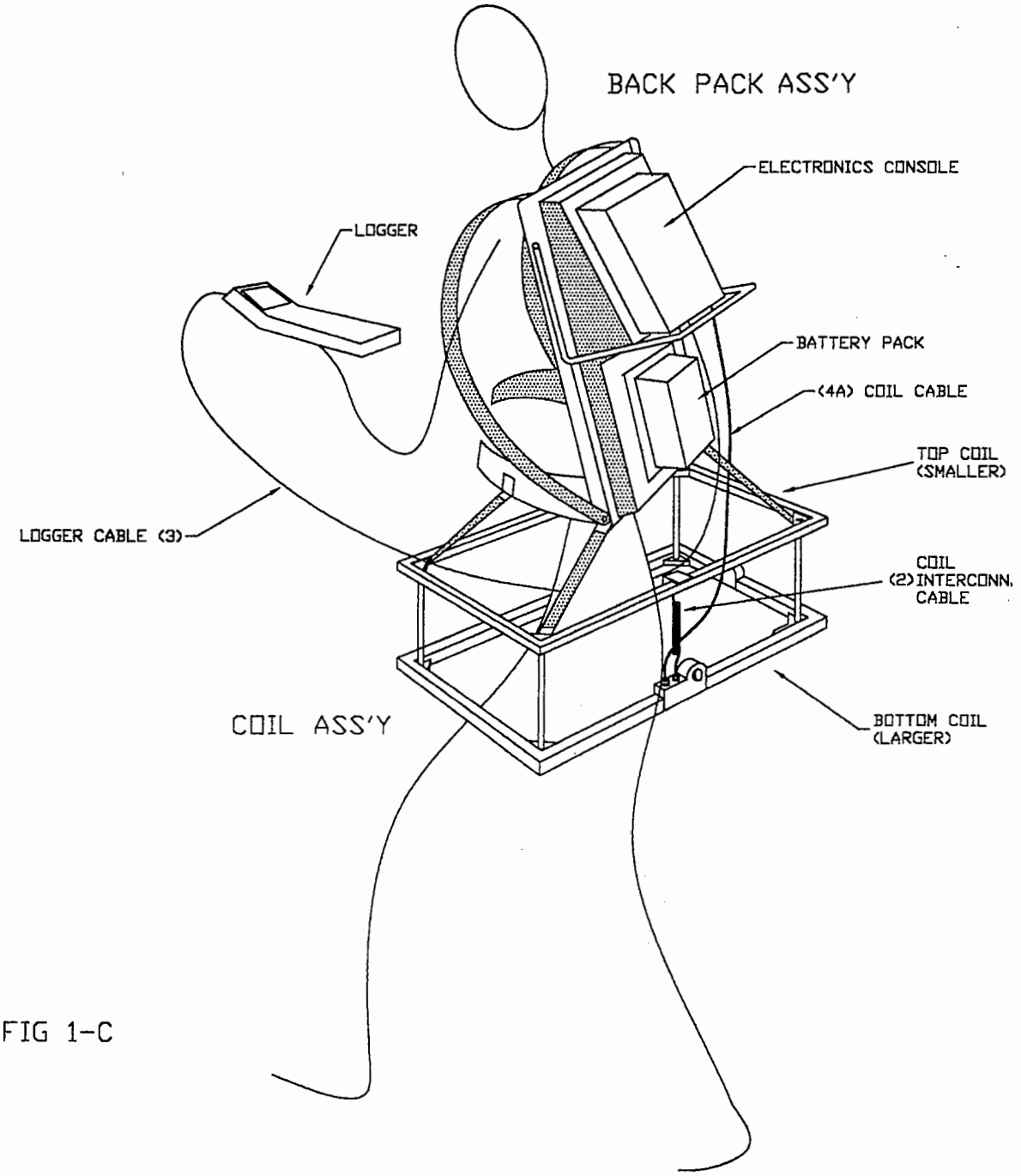
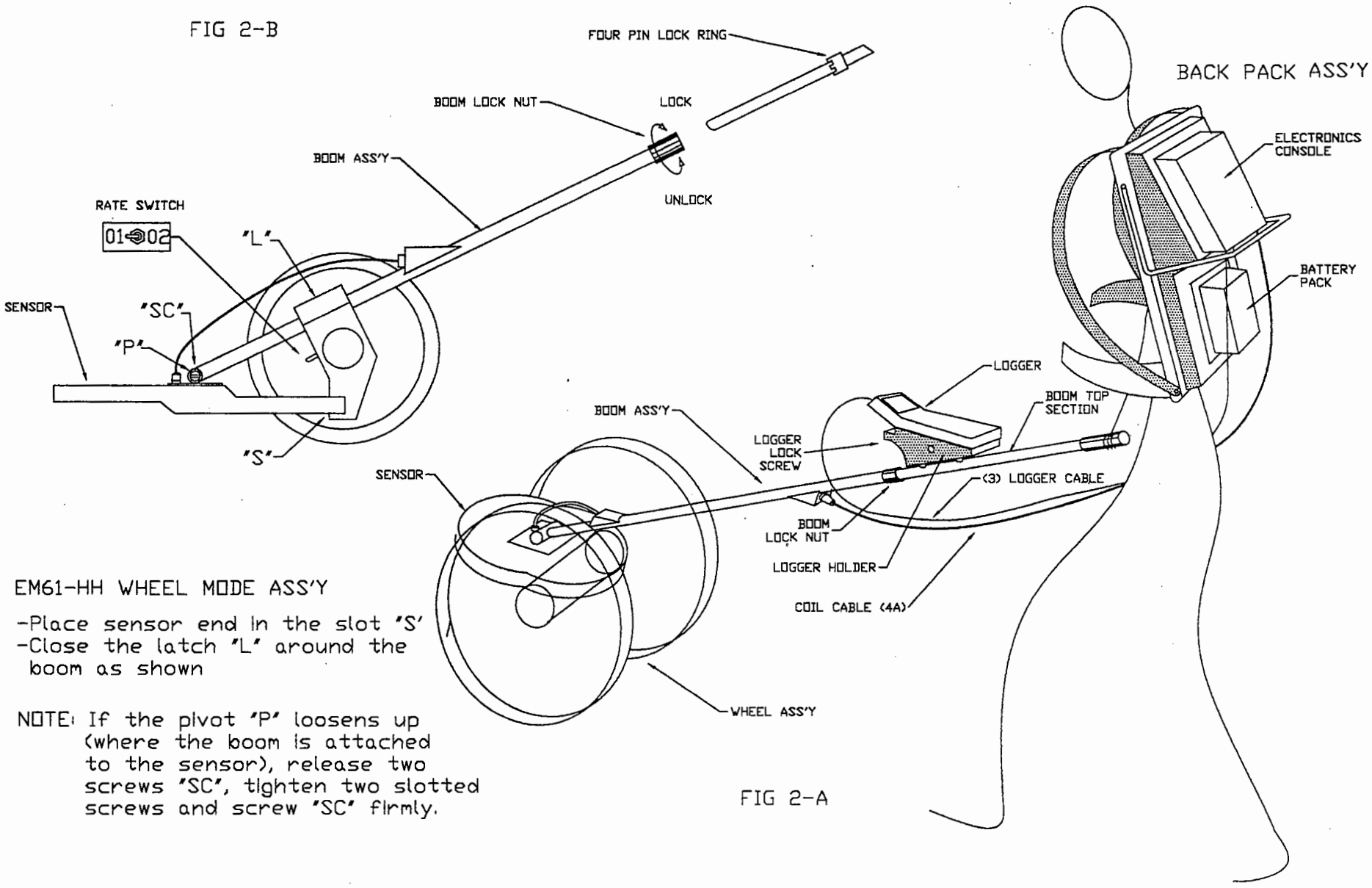

BACK PACK ASS'Y
ELECTRONICS CONSOLE
LOGGER
BATTERY PACK
(4A) COIL CABLE
TOP COIL
(SMALLER)
LOGGER CABLE (3)
COIL
(2) INTERCONN.
CABLE
COIL ASS'Y
BOTTOM COIL
(LARGER)

FIG 1-C

FIG 2-B



EM61-HH WHEEL MODE ASS'Y

-Place sensor end in the slot "S"
-Close the latch "L" around the boom as shown

NOTE: If the pivot "P" loosens up (where the boom is attached to the sensor), release two screws "SC", tighten two slotted screws and screw "SC" firmly.

FIG 2-A

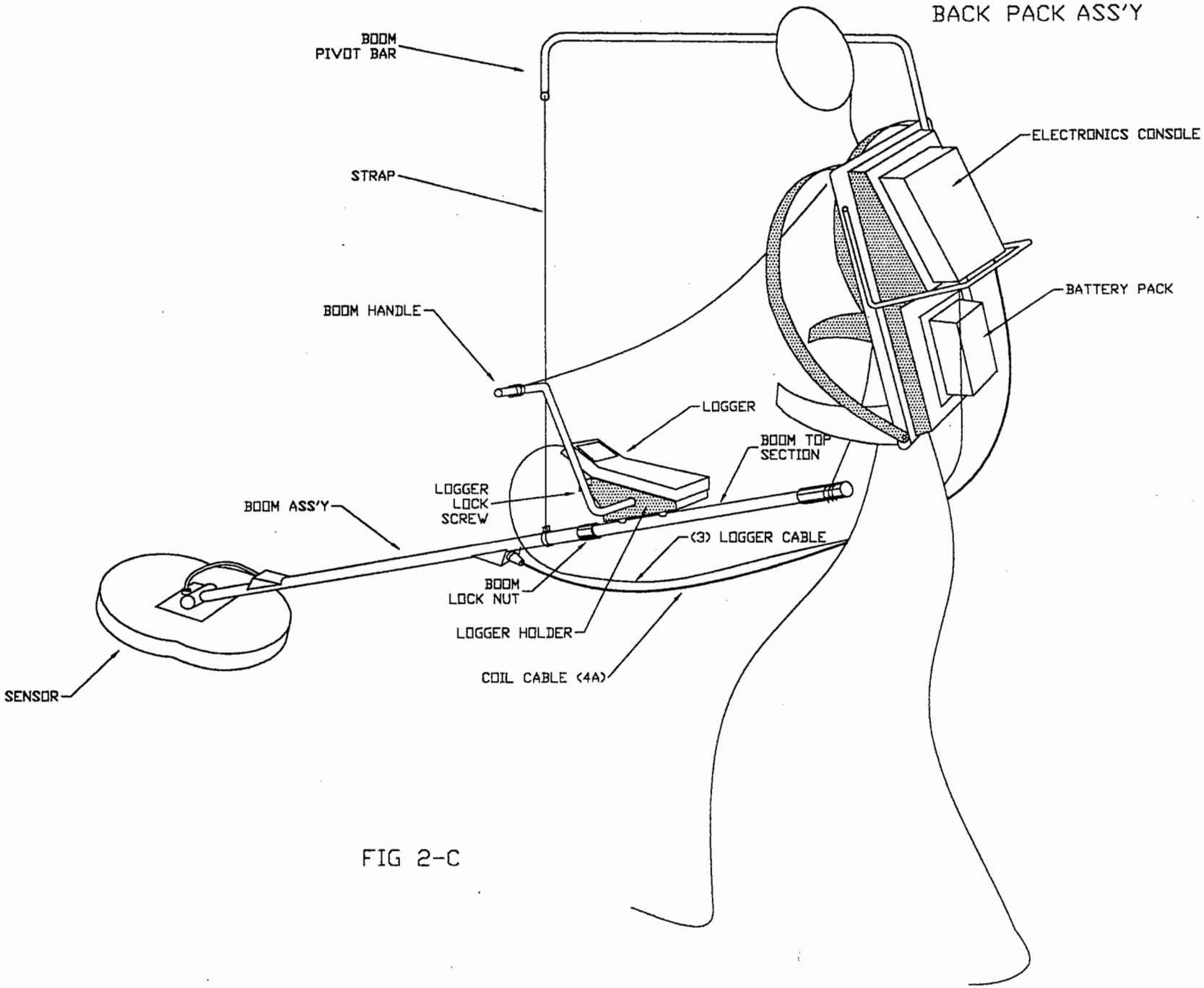

BACK PACK ASS'Y
BOOM PIVOT BAR
STRAP
BOOM HANDLE
ELECTRONICS CONSOLE
BATTERY PACK
LOGGER
BOOM TOP SECTION
LOGGER LOCK SCREW
BOOM ASS'Y
(3) LOGGER CABLE
BOOM LOCK NUT
LOGGER HOLDER
COIL CABLE (4A)
SENSOR

FIG 2-C

5 GPS Option

The EM61-MK2 system is designed for a direct interface with the GPS receiver. The EM61-MK2 controller (*Allegro)* with two serial ports and associated software allows direct interface to most of the standard format GPS receivers.

During the acquisition one port is receiving EM61 data, while the second port is simultaneously monitoring and recording data from the GPS receiver. Combined data set is stored in the same file inside the logger in the real-time.

Sections C and D of this manual give more detail on the GPS/EM61-MK2 operation. Note that an optional GPS Tripod that can be attached to the EM61-MK2 coil assembly is available from Geonics.

6. Console Battery

The instrument is supplied with two sets of rechargeable batteries. Each fully charged battery will last for about four hours of continuous operation. The battery pack is fixed to the backpack by three thumb screws and it is automatically connected to the console battery connector when it is placed in the appropriate place on the backpack. To check the battery voltage, interconnect console with the logger and go to **BATTERY CHECK** mode as described in the B section of this manual.

To determine if the battery will require charging or replacing soon, the battery voltage can also be measured with an external voltmeter. An advantage of using an external voltmeter is that the battery need not be installed in the system to obtain a voltage measurement.

If you are measuring the battery voltage with a voltmeter, you must insert the voltmeter probes correctly into the 3-socket connector on the battery pack front panel. If you inspect the connector closely you will notice that each socket is labelled with a letter. Insert the negative probe into the socket labelled A and the positive probe into the socket labelled C. (The A socket is also the system ground). Five ohms power resistor (~25W) across battery, will ensure that it is loaded with approximately the same load as the EM61-MK2 transmitter. This will give a more accurate measurement of the condition of the battery.

The fully charged battery will read above 13 V. Recharge the battery if its voltage is below 10.5 V.

The battery can be charged by attaching the battery charger to the connector on the battery cover. Remember to connect the charger to the battery before applying power to the charger. Completely charging a fully discharged battery takes 14 hours. To prevent defective charger from damaging power supply PCB, do not charge battery, when battery is connected to the EM61-MK2 console.

6.1 Console Battery Care

The console is powered by Pb/gel type of batteries. Pb/gel batteries work on the same

principle as Pb/acid batteries. Gel is used in the place of acid, and the batteries are sealed. As a result they can be shipped by parcel post as well as by passenger and cargo aircraft (cf. IATA Restricted Cargo Regulations, Article 1924).

The Pd/gel batteries can be fully recharged from total discharge several hundred times. If you typically use only a fraction of the battery capacity before recharging, the number of possible recharges increases.

The batteries maintain full capacity regardless of the pattern of use, but their capacity will eventually decrease with age.

From full charge, the batteries will lose 2 to 3% of their charge per month when stored at 20°C.

Deep Discharge Protection

The Dryfit battery, unlike conventional lead storage batteries, is protected against excessive discharge. In the event that a battery remains connected to a load for an excessive period of time, deep discharge protection ensures that the battery can be recharged without permanent damage. After 30 days of deep discharge, batteries should be recharged for a period of 48 hours. A completely discharged battery should not be left for longer than 30 days without recharging.

After recharge, it can be expected that the batteries will exhibit a loss in charge capacity, although this loss should not exceed 25% of original capacity. To recover lost capacity, batteries should be run through a series of (at least three) cycles of discharge and recharge.

Storage Conditions

It is important that the battery is stored fully charged. After use, set battery on charge and keep it on till next use. If not possible to keep battery continuously on charge, it should be stored fully charged at a mean ambient temperature of +20°C and be recharged after a maximum of 6 months. At higher temperatures, the period will be shorter, and at lower temperatures, will be extended. Since the specific gravity of the electrolyte will fall as the state of charge is reduced, causing the freezing point to rise, only full charged batteries should be stored at extremely low temperatures. Given that storage in the fully charged state has essentially positive effects on life and cycle resistance, it is recommended that self discharge should not be allowed to fall to below 50% of the charged state.

Batteries should be stored in a dry place.

7. Digital Recorder (Allegro) Batteries

The power consumption of the Allegro is very efficient. The Auto Suspend and Power Management features help to conserve power. Maintaining the battery pack and backup supply is simple.

There are three types of batteries and a backup capacitor associated with the Allegro:

- NiMH battery pack

- ❑ Battery holder for three alkaline cells (optional accessory)
- ❑ Internal lithium backup battery (powers the real-time clock and CMOS RAM)
- ❑ Super capacitor that serves as the RAM backup (maintains the RAM while you change the battery pack)

The battery pack is inserted at the factory. Do not remove it initially.

7.1 Main Power Source

The Allegro is powered by a rechargeable nickel metal hydride (NiMH) battery pack. The battery compartment is accessed through a door in the back of the case. **When you receive the Allegro, please note the following information about the batteries:**

– A NiMH battery pack is inserted into the Allegro before shipping. Immediately upon receipt of the Allegro, we recommend that you charge the battery pack for five hours using the AC power adapter. <u>There is no reason to remove the battery pack prior to charging it.</u>

By initially charging the batteries this way, you are able to become familiar with the Allegro's battery gauging feature and how the battery status LEDs work. This recommendation is made even if you eventually plan to use an external battery charger to charge the battery pack or if you are going to use the optional alkaline battery holder.

Prior to shipping the Allegro to you, the battery gauging is set, allowing the Allegro to know the pack's charge status. If you remove the battery pack and replace it, the charge status is unknown to the Allegro. Any time you insert a NiMH battery pack into the Allegro and then turn it on, a battery pop-up box asks you to enter the battery charge percent and capacity. These values must be set correctly for the battery gauging to work properly. Refer to *New Battery Popup Window* later in this section for details.

1) You can run the Allegro while it is charging.

2) Batteries should be charged at room temperature.

3) The NiMH battery pack must go through about three charge/discharge cycles before it can be charged to full capacity.

4) If you are using the optional alkaline battery holder in place of the NiMH battery pack, insert fresh cells into the battery holder and place the holder in the battery compartment (refer to the *Alkaline Battery Holder* instructions later in this section for details).

5) The first time you turn the Allegro on, it boots to Windows CE.

Details about battery life, recharging the battery pack, the battery status LED indications, power management features, and removing and inserting battery packs are located in this section of the manual.

Battery Life

Depending on your application, the batteries can last from 5 to 30 hours between charges (NiMH) or replacement (alkaline cells) as shown below:

Battery Pack	Capacity	Typical Operating Time
NiMH	3,800 mA hours	12 to 20 hours
Alkaline	1,600 mA hours	5 to 8 hours

The operating time stated above are based on a typical application where: the Allegro performance level is set to medium, the Power Manager is on, data are being entered manually on the keyboard, no external devices are powered by the Allegro, the backlight is used 10% of the time, and processing time is 20%. The actual operating time could vary from as little as 5 hours to as much as 30 hours, depending on your program and how the system is set up.

Recharging the NiMH Battery Pack

For applications where the Allegro is used for several hours each day, the NiMH batteries can be charged daily. The Allegro's built-in intelligent charging circuit manages the charging of the batteries and prevents them from being overcharged. For less frequent use, the batteries should be discharged below 80% before they are recharged for maximum battery life.

You should always be aware of the status of the main batteries before you go out into the field to collect data. The batteries may need to be recharged before you go. You need to take into account how much battery life is left and the amount of time required to charge the pack.

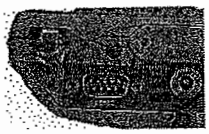
Temperature Ranges for Charging the NiMH Battery Pack

The Allegro's NiMH batteries are charged most efficiently at temperatures ranging between 10° to 20° C (50° to 68° F) when the AC power adapter is used. The Allegro batteries must be charged when the battery temperature is between 0° to 40° C (32° to 104° F) due to the nature of NiMH batteries. The chart below describes the Allegro battery charging behaviour at different temperatures

	Temp. Range Degrees C	Temp. Range Degrees F	Charging Behaviour
Recommended Charge Range	10° to 20°	50° to 68°	Most efficient; batteries charge withing 3 hours
Acceptable Charge Range	0° to 30°	32° to 86°	Batteries are charged within 4 hours
Too Cold Range	<0°	<32°	The batteries must reach 0° C (14° F) before they begin to charge
Too Hot Range	>30°	>86°	Battery charge cycle is complete in 4-5 hours. If the batteries have become too warm, they may only reach a 90 to 95% charge capacity

Try to charge the batteries within the recommended temperature range. If you need to charge the batteries in temperatures exceeding this range, you should purchase an extra battery for the most efficient operation of the Allegro.

Power Connector
A dedicated standard external DC power input connector is located on the top of the Allegro. The connector is 5.5 x 2.1 mm, 10 to 20 VDC. The AC power adapter and optional cigarette lighter power adapter are inserted into this connector.


< Power Connector

Charging Accessories for NiMH Battery Packs

- ❑ AC Power Adapter: Using the AC power adapter, the battery pack is recharged without removing it from the Allegro. Please note that you must use the adapter included with the Allegro or one that is capable of supplying adequate current (12 V at 1 Amp). Otherwise, your battery pack could be damaged. You can run the Allegro from the adapter while the batteries are being charged. Plug the AC charging adapter into an AC outlet and insert the connector into the external power input jack located on the top of the Allegro case. It may take up to five hours to fully charge a battery pack. When the batteries are fully charged, the charging circuit switches into trickle charge mode. You can leave the Allegro connected to the adapter continuously without overcharging or damaging the batteries.

- ❑ Cigarette Lighter Power Adapter (optional). With this adapter, you can charge battery packs via an automobile cigarette lighter. Plug the adapter into the

cigarette lighter and insert the connector into the external power input jack located on the top of the Allegro case. It takes from 3 to 5 hours to fully charge a pack. You can operate the Allegro with this adapter as well as charge the batteries.

- ❑ External Battery Charger (optional): The battery pack is removed from the Allegro to be charged using the external battery charger. Place the NiMH battery adapter on the charger. Slide the battery onto the charger and leave it for six hours. Refer to the instructions that came with the charger for more details. (Details on how to remove the battery pack are located later in this section of the manual).

Using Vehicle Power

It is important to have the Allegro in Vehicle Mode when it is connected to vehicle power, either directly or via the cigarette lighter power adapter. Vehicle Mode prevents excessive charging of the NiMH battery pack.

Using Vehicle Mode is necessary because every time the key is turned off the Allegro begins a new battery charge cycle. The Allegro circuitry detects when a battery pack is fully charged, however, it takes approximately twenty minutes for this to occur. Repeatedly attempting to charge a fully charged battery pack causes premature degradation in battery performance. In Vehicle Mode, charging is inhibited if the gauging circuitry indicates that battery pack is above 90% charged.

To put the Allegro in Vehicle Mode, follow these steps (the default is for Vehicle Mode to be off):

- From Windows CE: go to *Control Panel/Power Properties/Battery* and select the In-Vehicle Charge Mode option (Refer to *Allegro Owner's Manual, Section 4, Windows CE, Control Panel* for details).

- From DOS: go to the *System Setup Program/Power Management* screen and select "Yes" for the Vehicle Mode option (refer to *Allegro Owner's Manual, Section 5, MS DOS, System Setup Program* for details).

Resume Versus Reboot

The first time you turn the Allegro on after you receive it, the Allegro boots to Windows CE, the system default. Each time you replace the batteries, the Allegro *resumes* to the operating system it was in and the screen that was last displayed before the batteries were removed. Example: You are editing a Ptab document in Windows CE. To change the battery pack, you save the document but do not close it, turn the Allegro off, change the battery pack (within five minutes), and turn the Allegro back on. The Allegro automatically resumes to the Ptab document you were editing.

If the batteries are removed from the Allegro for longer than five minutes, the Allegro *reboots* to the last operating system it was in, but it does not resume to the screen that was last displayed before the batteries were removed. The Windows CE Desktop or the DOS prompt appears.

Battery Gauging

The Allegro's intelligent battery gauging circuit helps you efficiently maintain the batteries for your applications. The percentage of remaining charge in the batteries is indicated through the battery status LED indicators. The gauging works for both NiMH rechargeable batteries and alkaline batteries, although the mechanism is different, as outlined in this section.

- *Important Note: Battery gauging is provided as a tool to help you manage your batteries. It does not affect the performance of the Allegro or the batteries in any way. If the gauging circuitry is not properly synchronized with a NiMH battery, it may show erroneous readings. Please read this section on battery gauging so you understand the proper setup, functionality, and limitations of battery gauging.*

How Battery Gauging Works for the NiMH Rechargeable Battery

The Allegro employs a circuit that watches how much charge is added to or removed from the rechargeable battery. To illustrate how this circuit works, imagine the battery as a tank of water. The battery capacity is like the size of the tank in gallons. Watching charge is like watching how many gallonsof water flow into or out of the tank. Gauging the battery is like gauging how full the tank is, without being able to see into it. You must know the size of the tank and how full it was to start with to determine the amount of water in the tank. As water flows out of the tank, the percent full can be calculated by subtracting how much water has flowed out of the tank from the starting point and then dividing by the capacity of the tank. This is exactly what the Allegro does, except it monitors milliamp-hours of electric charge instead of gallons of water

For the battery gauging to work correctly on the Allegro, the following values must be known about the NiMH battery pack:

- Charge percent
- Capacity

The battery gauging is set in the following ways:

1) The charge percent and capacity values are set at the factory for the battery pack. Once you fully charge the battery pack using the AC charging adapter (the pack is shipped in a discharged state), the gauging is automatically set correctly. You do not need to set it manually

2) When you remove and insert a battery pack, a popup window appears asking you to select the charge percent and capacity. The popup window is described later in this section under *Setting Battery Gauging From the Battery Popup Window.* Please note that if either of these values are incorrect, the gaugin is not accurate.

The battery gauging is an estimate. It works well in applications where the Allegro is used and charged every day. When it is not used much and goes several days between charges, the gauging may not be as accurate in reflecting the tru charge of the battery pack. The accumulated error can be up to 5% per day. To avoid errors, keep the Allegro attached to the AC charging adapter when you are not going to use it for a few days. This practice prevents the battery pack from self-discharging. The battery stays

fully charged and the battery gauging reflects the correct status of the battery pack.

How Battery Gauging Works When Using Alkaline Batteries
Alkaline batteries have a better slope to the voltage discharge curve than NiMH batteries. Because of this, the voltage can be read directly to gauge the battery charge percent.

The gauging may vary depending on the grade and brand of the batteries being used. For best results, we recommend you use the new types of alkaline batteries such as the Duracell Ultra™ and Energizer Tiitanium™ . Also, temperature and loading affect alkaline battery voltage and may cause the gauging to behace differently in different environmental conditions. When moving from a cold environment to a warm one the battery charge LED indicators may move up instead of down. This happens because in cold temperatures alkaline batteries have less charge capacity than in warm temperatures and this is reflected in the voltage output.

Battery Status LED Indicators

There are five LEDs. Depending on which LED is lit, starting left and moving right, the battery charge remaining is as follows:

LED	Status	Indicator	Battery Charge Remaining
1	Blinking	Low Voltage	0 to 10%
1	Steady Light	Charge Flow	10% to 20%
2	"	"	20% to 40%
3	"	"	40% to 60%
4	"	"	60% to 80%
5	"	"	80% to 100%

♦ *Important Note: The LED indicators are meant to give only an approximate indication of battery charge remaining, not an exact reading.*

When the battery charge drops to 10%, the voltage begins to drop off rapidly. When the Allegro detects this low battery condition, the battery status LED indicator farthest to the left begins to blink to let you know it is time to recharge or replace the batteries. You have from ten minutes to one hour (depending upon power consumption rate) to save you data and exit your program.

When the battery pack voltage drops sufficiently, the Allegro automatically goes into suspend mode. Charge or replace the batteries as soon as possible. The battery pack has enough charge left to retain the system RAM for a short period of time, at which point the Allegro completely powers down to prevent damage to the batteries. If this happens, the Allegro reboots after you charge or replace the batteries. Any data that were not saved to disk are lost.

Charging Indicator

When the rechargeable batteries are being charged via the AC power adapter or the vehicle cigarette lighter power adapter, the LED underneath the charging indicator is lit. When the batteries are fully charged, the LED turns off. Note that when the LED turns off, the batteries continue to receive a trickle charge.

If the charging indicator LED does not light up when you plug the Allegro into a charger, the battery has a 90% or higher charge and does not need to be charged. Batteries should be discharged below 80% before they are recharged for maximum battery life.

Windows CE Battery Status Icons - WIN CE

In addition to the LED indicators, when you are in Windows CE icons appear on the Taskbar in the system tray that indicate the battery status of the main battery and the CMOS battery.

 Batteries are charging while the Allegro is being operated

 Powered by the battery pack, charge is low

 Powered by the battery pack, charge is very los

 CMOS backup battery is low

Power Management Features

To conserve power, the Allegro has the following built-in power management features: Auto Suspend and Power Manager. These features are controlled through the *Control Panel/Power Properties* program in Windows CE and the *System Setup Program/Power Management* screen in DOS.

Auto Suspend

When the Auto Suspend feature is on, the Allegro turns itself off if there is no activity after a specified period of time. The time ranges are from 5 to 75 minute increments. Auto Suspend monitors both keystrokes and processor activity.

Power Manager

The BIOS Power Manager is a sophisticated mechanism which automatically speeds up and slows down the system CPU based on the level of activity. Activities monitored include keypresses, serial port activity, changes to video memory, file system activity, and PC card activity. When there is a high degree of activity, the system runs at a faster rate. When there is a lesser degree of activity, the system runs at a slower rate, consuming less power. If the Power Manager is enabled, the CPU Performance setting affects the range of speeds at which the CPU runs. When the Power Manager is turned off, the CPU Performance setting causes the CPU to run at a fixed clock speed.

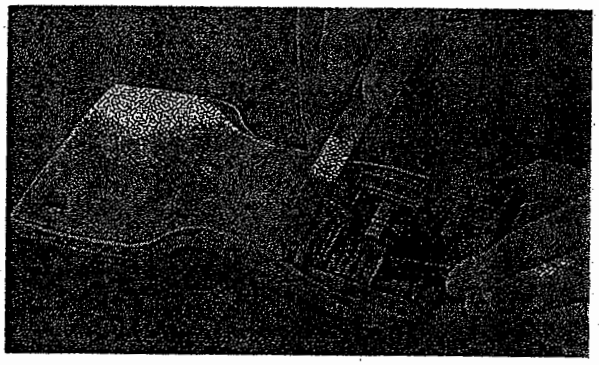
In Windows CE, the Power Manager is built-in. In DOS, you can leave it on (default) or turn it off. Because the Power Manager can greatly extend the life of the batteries, we recommend that you run the Allegro with the Power Manager on and the CPU speed set to medium.

You can gain even more power management efficiency within your application program by following the recommended power management techniques discussed in *Section 7 and Section 8* of the Allegro Owner's Manual.

NiMH Battery Pack: Changing and Setting Gauging

The battery compartment is accessed through door in the back of the case. To open the battery compartment door, push up on the release latches on the sides of the case. The door pops open. When you close the battery compartment door, the latches automatically lock the door into place and seal the compartment. Make sure that the slide latches are completely closed.

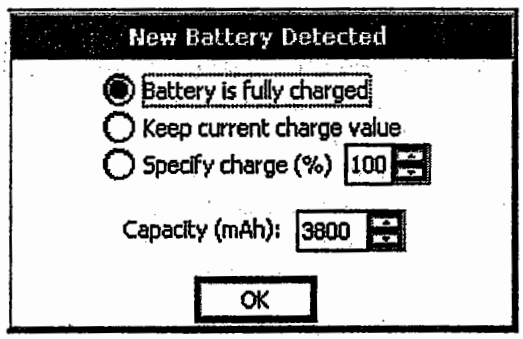
Before you remove an existing battery pack from the Allegro, exit from open programs and turn the Allegro off. To remove a battery pack, slide it towards the left side of the battery compartment and pull it out. To insert a NiMH battery pack, place it in the left side of the battery compartment and slide it all the way to the right.



Setting Battery Gauging From the Battery Popup Window

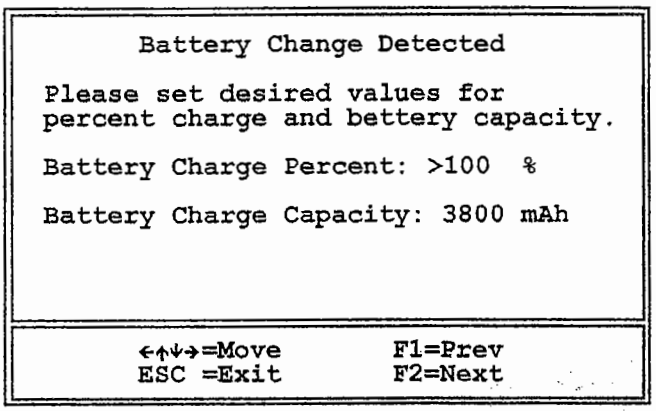
Whenever a NiMH battery is inserted into the Allegro and it is turned on, a popup window is shown directing you to select values for battery charge percent and battery charge capacity. These values must be set correctly for the battery gauging function to work properly, as outlined earlier in this section of the manual.

If you are in Windows CE, the following window is shown:



If the *Battery is fully charged option* is selected, the charge percent defaults to 100%. If the *Keep current charge value* is selected, the charge percent shown reflects the charge percent of the previous battery.

If you are in DOS, the window appears as follows:



Setting the Battery Charge Percent

Based on the status of the battery pack, follow the recommendations below to set the battery charge percent. (In Windows CE press the arrow keys to increment the numbers up or down. In DOS, use the <F1> and <F2> function keys).

	Correct Selection/Setting	
Battery Status	Windows CE	DOS
Fully charged	Battery is fully charged	100% (default)
Removed and replaced without charging	Keep current charge value	Last
Uncertain, can estimate	Select charge from 10 to 100%	Select charge from 10 to 100%
Uncertain, can't estimate	See suggestions that follow	See suggestions that follow

If you insert a battery pack and do not have a good idea what the status of it is, we recommend that you do one of the following:

1) Set the charge to 10%, plug the Allegro into the AC wall charger, and fully charge the pack for 3 to 5 hours. Once the battery pack is fully charged, the gauging is automatically set to 100% and the battery LED indicators accurately reflect the battery charge.

2) Say okay to the default setting (battery is fully charged). Initially the 5th LED is lit. Depending on the actual battery charge percent, you could see it jump rapidly to the first LED. When this LED begins to blink, fully charge the battery. Once the battery pack is fully charged, the gauging is automatically set to 100% and the battery LED indicators accurately reflect the battery charge.

Setting the Battery Charge Capacity

The Charge Capacity field should be set to the charge capacity of the newly installed battery pack in milliamp-hours (mAh). The charge capacity of the NiMH batteries we have provided for the Allegro are as follows:

Gold Peak™ (GP) VR151	3800 mAh
Empire™	3500 mAh
Duracell™ DR9	3000 mAh

If you purchase a battery pack from another vendor, note what the capacity is. For optimum performance, it is best to use battery packs with a 3000 to 4000 mAh capacity. The higher the capacity of the battery pack, the longer it holds a charge. Battery packs with a capacity over 4000 mAh do not charge fully.

As a battery pack ages, it does not operate as long on a charge as it did when it was new. The capacity could be reduced by as much as 50% at the end of its useful life. Over time, the capacity setting for an individual battery pack may need to be adjusted downward to account for age.

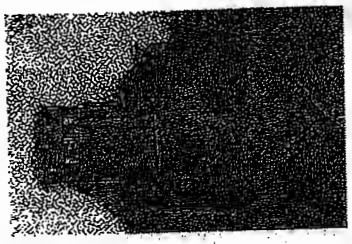
Alkaline Battery Holder: Inserting Batteries and Usage Information

The alkaline battery holder enables you to power the Allegro Field PC with alkaline batteries. Follow the steps outlined below for proper usage.

1) Exit from any open programs and turn the Allegro off before changing the batteries.

2) The Allegro battery compartment is accessed through a door in the back of the case. To open the compartment door push up on the release latches on the sides of the case. The door pops open. Remove the NiMH pack or alkaline holder by sliding it to the left and pulling it out.

3) Open the door to theh alkaline battery holder by pressing in on both tabs with your index finger and thumb as shown.



4) Insert three fresh AA alkaline batteries, taking care to orient them correctly (only use alkaline batteries). Always replace all three batteries at once. (Note: For best results, we recommend that you use the new types of alkaline batteries such as the Duracell Ultra™ and Energizer Titanium™.)

5) Slide the door to the alkaline holder back into place, making sure it snaps securely shut.

6) Place the alkaline battery holder in the left side of the Allegro battery compartment. Put gentle pressure on the holder while sliding it all the way to the right.

7) Press down on the Allegro battery compartment door to close it. The latches should automatically lock the door into place and seal the compartment. Make sure that the slide latches are completely closed.

8) While you are using the Allegro Field PC, occasionally check the battery LED indicators above the Allegro display. When the battery power gets low, replace the alkaline batteries or insert a NiMH pack.

Important Information Regarding the Use of Alkaline Batteries

The Allegro Field PC is designed to be used with the rechargeable NiMH battery pack that came with the unit. The alkaline battery option should be considered as a backup to the NiMH battery pack, not as the main source of power for an extended period of time. Alkaline batteries have a lower capacity and a higher resistance than NiMH batteries. Thus the battery life and performance of the Allegro are reduced when alkaline batteries are used. The Allegro runs as described below:

- ❑ The clock speed automatically switches down to a maximum speed of 33 MHz
- ❑ The display heater cannot be used
- ❑ As the batteries are drained, the Allegro automatically switches to a slower clock speed and limits the backlight intensity to further reduce power consumption and prevent the unit from turning itself off because of power demands
- ❑ Battery life ranges between 2 and 8 hours (this is highly dependent on the temperature)

If you have been using alkaline batteries in the Allegro and switch to a NiMH battery pack, the clock speed and backlight brightness setting automatically return to the levels they were previous set at.

Storing the Allegro During Inactive Periods

To protect the Allegro and your files during long or short-term storage periods, please take the following precautions:

- Save all data and programs you want to keep to disk.
- Store the Allegro in a cool location (<20°C, 68°F).

Your data and programs are secure as long as they have been saved to disk, even if the batteries become discharged. The data storage disk is non-volatile. It does not depend on the battery to store the data for extended periods.

Storing the Allegro for Less Than Two Months

If you store the Allegro for less than two months, we recommend that you leave the NiMH battery pack in the Allegro and attach the AC power adapter to keep the batteries charged. Once the battery pack is fully charged, the Allegro switches to trickle charge mode. You can leave the Allegro in trickle charge mode continuously without damaging the batteries. The battery pack will be fully charged when you are ready to use the Allegro.

Storing the Allegro for More Than Two Months

If you store the Allegro for more than two months, remove the battery pack and attach the AC power adapter to prevent the internal lithium backup battery from draining. When you are ready to use the Allegro, insert a battery pack and fully charge it if necessary.

NiMH Battery Pack's Useful Life

Battery packs can be recharged approximately 600 times before they need to be replaced. This is dependent on the temperatures they have been exposed to, operating conditions, and charging and discharging practices.

Recycling the NiMH Batteries

The NiMH batteries inside the Allegro battery packs are recyclable. We are voluntarily participating in an industry program to collect and recycle these batteries when they are taken out of service in the United States or Canada. The recycling program provides a convenient alternative to placing used NiMH batteries into the trash or the municipal waste stream. Our involvement in this program is part of our commitment to preserving our environment and conserving our natural resources.

Because most battery recycling bins available for public use do not accept NiMH batteries, you are welcome to return the spent battery packs used in the Allegro to our office and we will recycle the batteries for you. If you plan to do this, please contact us for information on how to properly package and ship the batteries.

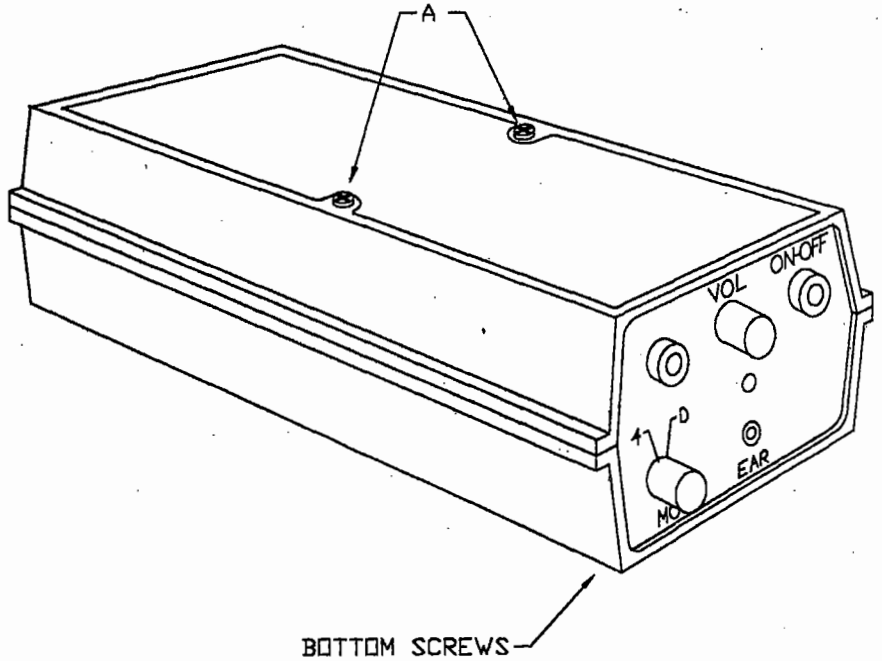
Spare NiMH Battery Packs

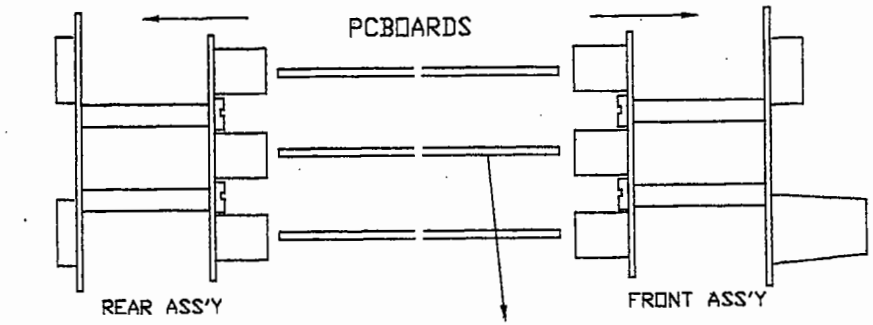
Spare battery packs should be stored in a cool location. Avoid placing battery packs "contact side" down on a metal surface. Also, do not stack packs so that their contact touch one another. These practices will cause the batteries to drain. The shelf-life of a battery pack is about two months. Before using a spare pack, you should charge it.

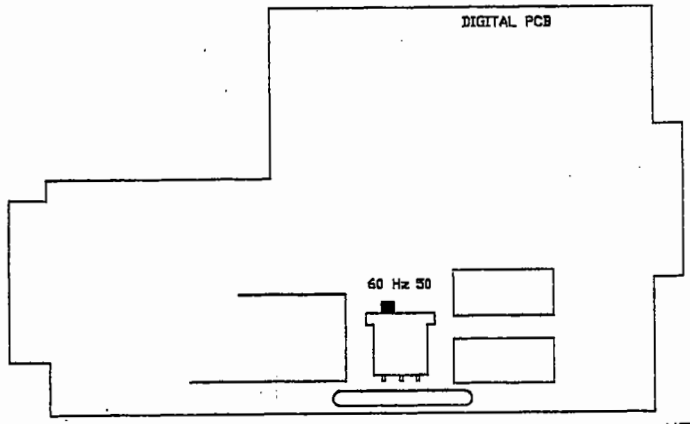
7.2 Short-Term Back Supply

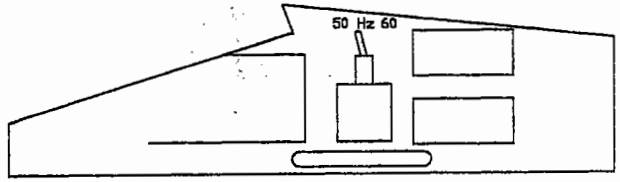
The Allegro has a super capacitor that behaves like a backup battery. When the main batteries are removed, the capacitor maintains the RAM for up to 5 minutes, allowing you plenty of time to change the batteries. The capacitor cannot operate the Allegro.

50-60 Hz SWITCH









NOTE:
TWO VERSIONS
OF SWITCHES

- REMOVE TWO SCREWS-A
- REMOVE FOUR BOTTOM SCREWS
- LIFT THE TOP COVER
- LIFT ALL PC BOARDS OUT OF BOTTOM COVER
- PULL OUT FRONT AND REAR PANEL ASS'Y
- 50-60 Hz SWITCH IS ON DIGITAL PCB AS SHOWN
- ASSEMBLY THE UNIT IN REVERSE ORDER

EM61-MK2
GEONICS LTD

FIG 2D.

The capacitor is charged by the batteries. It holds a charge as long as the batteries or external power are supplied. When a battery pack is replaced, the capacitor charges up to full capacity in about 2 minutes.

If power is not supplied to the Allegro for more than 5 minutes, the Allegro reboots when the battery pack is replaced or charged. All the programs, data, and applications saved to the disk are safe. Information that was not saved to the disk is lost.

The super capacitor should not need replacement through the life of the Allegro.

7.3 Backup Battery, Real-Time Clock

A 3.6 V lithium backup battery supplies current to the Allegro to maintain the real-time clock when power is not supplied to the Allegro. This battery should last for at least 5 years.

Replacing the Lithium Backup Battery

If the Allegro does not hold the date and time or you get a CMOS error message, the lithium battery needs to be replaced. You can check and see whether or not the lithium battery is good or bad. In Windows CE, go to *Control Panel/Power Properties/Battery.* Additionally, when it is low, the following icon appears in the system tray on the Windows CE Desktop  .

In DOS, go to *System Setup Program/System Information Screen* to view the status of the lithium battery.

You must return your Allegro to the factory for lithium backup battery replacement.

8. 50 Hz/60 Hz Operation

The EM61-MK2 is designed for maximum rejection of power line interference. By proper selection of instrument repetition rate; 75 Hz for operation in countries with 60 Hz power line frequency and 62.5 Hz for operation in countries with 50 Hz power line, most but severe power line noise will be rejected by the instrument. EM61-MK2 repetition rate is normally set in the factory according to the country that the instrument was originally intended to be used. If the condition has changed, an internal switch allows changing the operation rate as shown in Figure 2D.

9. EM61-MK2 Technical Specifications

Measured Quantity	:	Four channels of secondary response in mV	
EM Source	:	Air-cored coil, 1 x 0.5 m size	
Current Waveform	:	Unipolar rectangular current with 25% duty cycle	
EM Sensors	:	Bottom coil:	Air-cored coil, 1 x 0.5 m in size, coincident with EM source
	:	Top coil:	Air-cored coil, 1 x 0.5 m in size 28 cm above main coil
Maximum Output	:	10 000 mV	
Dynamic Range	:	18 bits	
Time Gates	:	Four gates of bottom coil response only, centered at 256, 406, 706 and 1306µsec; or, three gates of bottom coil response at 256, 406 and 706µsec, with one gate of top coil response at 706µsec, after T/O time.	
System Controller	:	Allegro field computer with 486 AMD processor, 24-line LCD display with 40 characters per line.	
Acquisition Speed	:	Up to 16 records (4 time gates per record) per second	
Data Storage	:	24MB solid state memory for up to 1,000,000 records; extended memory, optional	
Power Supply	:	12 V rechargeable battery for 4 h continuous operation	
Operating Weight	:	Backpack:	8 kg; 60 x 30 x 20 cm
& Dimensions	:	Coil Assembly:	14 kg (23 kg trailer mode)
		Bottom:	100 x 50 x 5 cm
		Top:	100 x 50 x 2 cm
Shipping Weight & Dimensions	:	38 kg (70 kg with trailer) 108 x 60 x 25 cm (Box 1; harness mode only) 54 x 54 x 52 cm (Box 2; with trailer option)	

Optional

Hand-held Sensor

Time Gates	:	Four gates of bottom coil response only centered at 147, 263, 414 and 613µs; or three gates of bottom coil response at 147, 263 and 414µs with one gate of top coil response at 414µs sec after turn-off time
Sensor Size	:	33 x 20 cm
Wheel Mode Resolution	:	0.1 or 0.2 meters, switch selectable

Weight	:	With wheels	7.5 Kg
		Without wheels	2.8 Kg
Length	:	Minimum	130 cm
		Maximum	180 cm

A1. EM61-MK2HP

8. Operating Notes

The EM61-MK2HP is a high power version of Geonics EM61-MK2 Metal Detector. It provides up to 8 times more target response than the standard unit, resulting in a significant increase in signal-to-noise ratio.

The following section is a note describing the functions of the EM61-MK2HP that differ from the operation of the standard EM61-MK2, as described in this manual.

(a) Output Power Switch

The EM61-MK2HP unit can be operated at two output power levels; a) standard power level (LO) and, b) high power level (HI). The difference in the transmitted signal between two modes is a factor of two, two times higher in "HI" position. For the maximum output signal set the Power Mode Switch located on the side of the battery pack, to the "HI" position.

For a survey that does not require maximum output power, set the Power Mode Switch to the "LO" position. With the switch in the "LO" power position the battery will last approximately 4 times longer than if the switch is in the "HI" position.

Important:

Prior to changing the power mode from "HI" to "LO" (or "LO" to "HI") the circuit breaker on the backpack should be in the "OFF" (pulled out) position.

(b) Two Battery Option

There are two types of batteries which can be used with this unit (normally only the high power type is supplied). A large capacity battery (32 Ah) which supplies power for approximately two-and-a-half hours in the high power mode and about 7 hours in the low power mode, and a small capacity battery (10 Ah) that will provide for about two-and-a-half hours in the low power mode. The small battery pack can only be used in the low power mode.

Figure 2HP shows the assembly procedure for both types of batteries. Note that the larger battery is substantially heavier than the smaller one; 13 kg compared with 4.5 kg, therefore the decision on which battery to use will depend on the availability of the battery, length of survey and the desired output power.

(c) Charging High Power Battery Pack

When charging the high power battery pack the Power Mode Switch (LO/HI) on the battery pack has to be in the "LO" position.

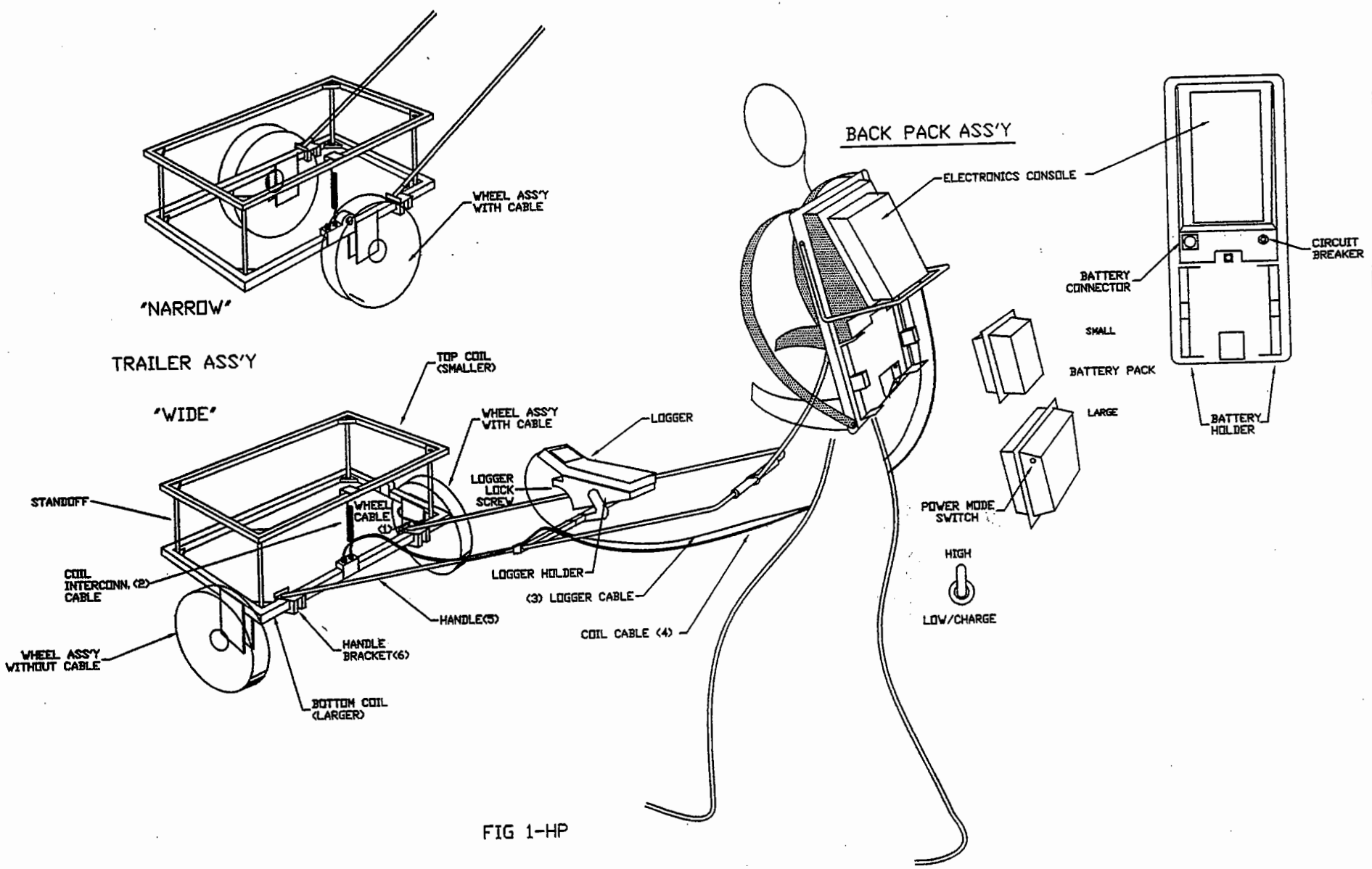
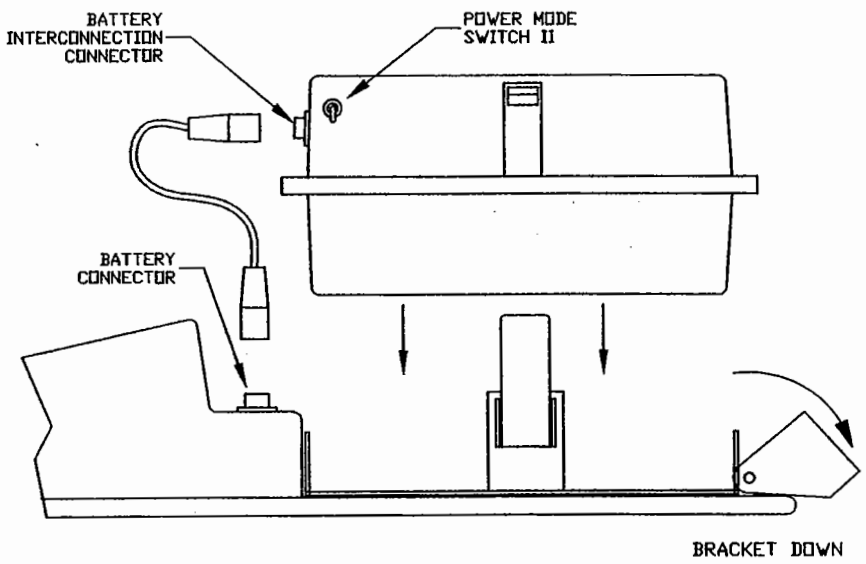

"NARROW"
WHEEL ASS'Y WITH CABLE
TRAILER ASS'Y
"WIDE"
TOP COIL (SMALLER)
WHEEL ASS'Y WITH CABLE
LOGGER
LOGGER LOCK SCREW
STANDOFF
WHEEL CABLE (1)
COIL INTERCONN. (2) CABLE
LOGGER HOLDER
(3) LOGGER CABLE
HANDLE(5)
COIL CABLE (4)
WHEEL ASS'Y WITHOUT CABLE
HANDLE BRACKET(6)
BOTTOM COIL (LARGER)
BACK PACK ASS'Y
ELECTRONICS CONSOLE
CIRCUIT BREAKER
BATTERY CONNECTOR
SMALL
BATTERY PACK
LARGE
BATTERY HOLDER
POWER MODE SWITCH
HIGH
LOW/CHARGE

FIG 1-HP

TWO BATTERY OPTIONS

A. LARGE BATTERY PACK



B. SMALL BATTERY PACK

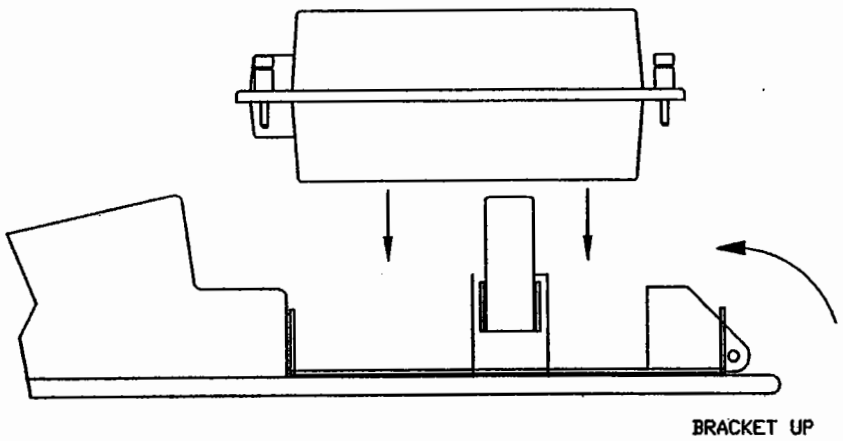
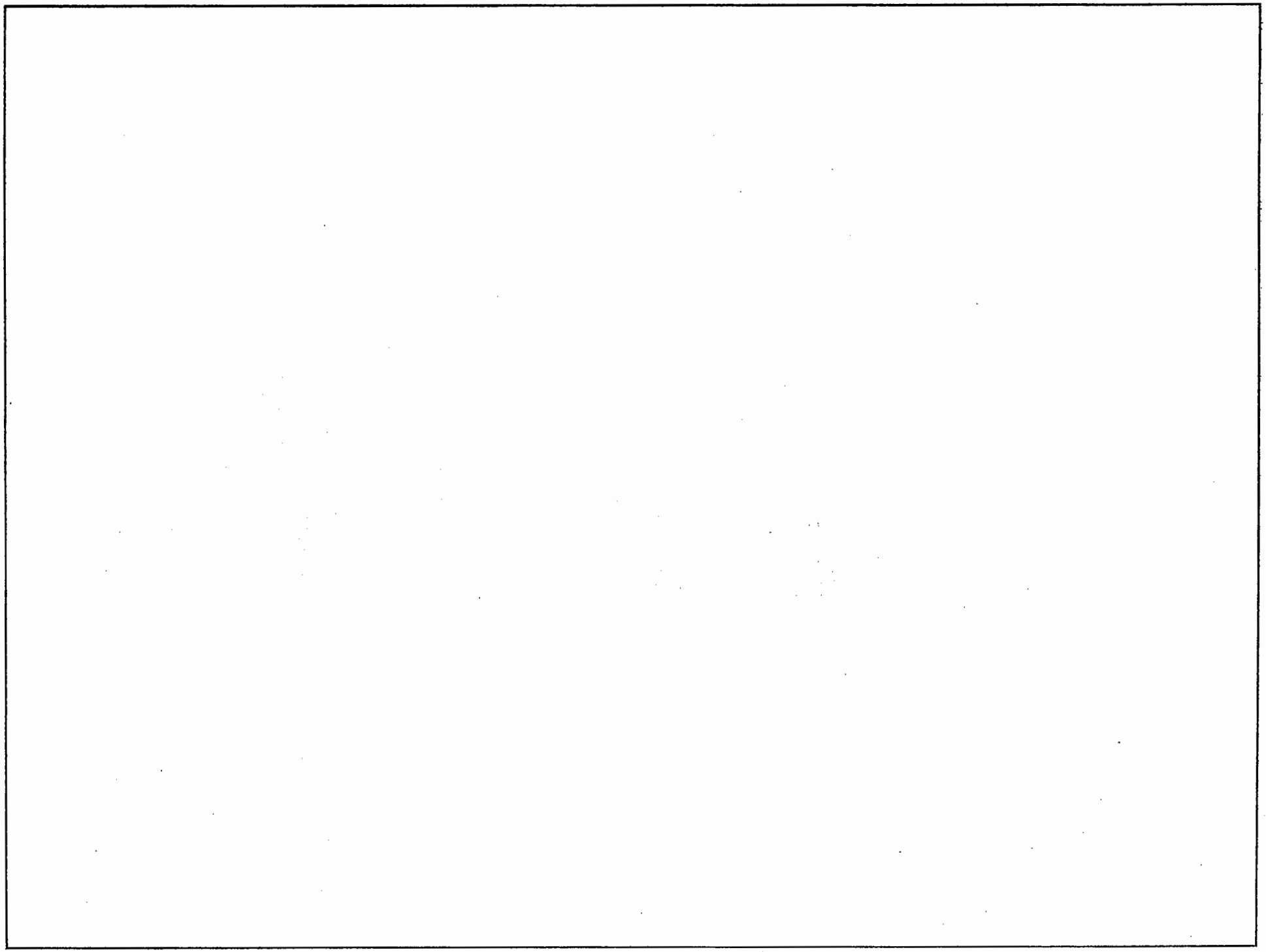


FIG 2-HP

2. EM61-MK2HP Technical Specifications

Measured Quantity	:	Four channels of secondary response in mV
EM Source	:	Air-cored coil, 1 x 0.5 m size
Current Waveform	:	Bipolar rectangular current with 25% duty cycle
EM Sensors	:	Bottom coil: Air-cored coil, 1 x 0.5 m in size, coincident with EM source Top coil: Air-cored coil, 1 x 0.5 m in size 28 cm above main coil
Maximum Output	:	10 000 mV
Dynamic Range	:	18 bits
Time Gates	:	Four gates of bottom coil response only, centered at 261, 376, 527 and 727 µs; or, three gates of bottom coil response at 261, 376 and 527µsec, with one gate of top coil response at 527µsec, after T/O time.
System Controller	:	Allegro field computer with 486 AMD processor; 24-line LCD display with 40 characters per line
Acquisition Speed	:	Up to 16 records (4 time gates per record) per second
Data Storage	:	24 MB solid state memory for up to 1 000 000 records; extended memory optional
Power Supply	:	Two 12 V/16 Ah rechargeable batteries or 12 V/10 Ah rechargeable battery (for low power operation only) • 2 h continuous operation in full power mode • 7 h continuous operation in low power mode • 2 h continuous operation in low power mode (small battery)
Operating Weight & Dimensions	:	Backpack: 21 kg; 60 x 30 x 20 cm Coil Assembly: 14 kg (23 kg trailer mode) Bottom: 100 x 50 x 5 cm Top: 100 x 50 x 2 cm
Shipping Weight & Dimensions	:	92 kg (103 kg with trailer) 108 x 60 x 25 cm (Box 1; harness mode only) 54 x 54 x 52 cm (Box 2; with trailer option)



A2. EM61-MK2 (MK1) CALIBRATION DEVICE (QC COIL)

1. Introduction

An optional standard calibration device that can be used to check the gain calibration of Geonics Limited EM61-MK2 (MK1) UXO Detector is available. The device can be used as an "absolute" calibration, so that the different EM61 units, if calibrated with the QC coil, would under the same conditions give the same results over a particular target.

2. Description

The EM61 calibration device is used to check the operation of the complete EM61 system including transmitter and both receiver coils, as well as the signal processing console.

Two types of QC coils are available: a. external and, b. internal. The external device is mounted on the side of the main (bottom) coil as per Figure 3a. It is a self-contained unit and can be used on the different units without any modification of the EM61. The internal calibration device, as per Figure 3b., uses the internal component of the receiver coil for operation and, therefore, requires system (coil) modification at Geonics manufacturing facility.

The advantage of the internal device over the external one is a smaller size and a somewhat lower cost, assuming that modification is performed prior to delivery of new units, or on the units at Geonics for repair or recalibration. Either device can be used with the EM61-MK1 or MK2 in two different modes: a. by following EM61 logger instructions, where the logger will determine, if after activating the calibration check, the reading is inside the standard values within ± 5% tolerances, and it will indicate if the instrument has passed the calibration test or not, or b. by comparing the value recorded during the calibration check with the standard value as per supplied table, - Table I.

Either device can be used with all three EM61 configurations: EM61-MK2 with either 1 x 0.5 coil or 1 x 1 m coil and EM61-MK1 with 1 x 1 m coil.

3. Calibration Procedure

The calibration check procedure is as follows:

a. External Device

The instrument under test should be placed outdoors as for normal operation far from any larger metallic object. After the instrument nulling, the red button on the calibration device that is mounted inside of the main (bottom) coil - Figure 3a., should be pressed and held for about three to five seconds. The logger program or comparison with the standard table will determine if the unit is operating properly. We suggest that ± 5% deviation from the standard value is considered acceptable.

b. Internal Device

The procedure is similar to the external device, except that the internal device is

mounted on the side of the coil connector box and it has two buttons: one for the bottom coil check, and one for the top. The standard value for the internal and external devices are different, due to the different geometry and components used for two devices.

4. Table I of the Standard Value

1. EM61-MK2 with 1 x 0.5 m Coil

	A. External QC Coil	B. Internal QC Coil
CH 1	- 3935 mV	- 4608 mV
CH 2	- 3660 mV	- 3574 mV
CH 3	- 2486 mV	- 2096 mV
CH 4	- 1235 mV	- 784 mV
CH T	- 386 mV	- 708 mV

2. EM61-MK2 with 1 x 1 m Coil

	A. External QC Coil	B. Internal QC Coil
CH 1	- 1052 mV	- 694 mV
CH 2	- 929 mV	- 533 mV
CH 3	- 644 mV	- 319 mV
CH 4	- 320 mV	- 120 mV
CH T	- 64.2 mV	- 81 mV

3. EM61 with 1 x 0.5 m Coil

	A. External QC Coil	B. Internal QC Coil
CH B	- 2300 mV	- 2008 mV
CH T	- 324 mV	- 590 mV

4. EM61 with 1 x 1 m Coil

	A. External QC Coil	B. Internal QC Coil
CH B	- 540 mV	- 293 mV
CH T	- 52 mV	- 67 mV

5. External QC Coil Mounting

To mount the external QC coil, set it tightly against the corner of the EM61 bottom coil, and mark the drilling hole using two holes on the QC coil as a guide. Drill using #10 (5 mm diameter) drill bit through the support corner. Use two supplied stainless steel screws to fix the Q coil on the bottom coil. It is very important that the QC coil is mounted on the bottom coil in such a way that it sits tightly against all three sides of the bottom coil corner. Even a small gap between the QC coil and the bottom coil corner will introduce an error in the test reading.

6. EM61-MK2 Recalibration

In case the QC coil test readings are outside the standard values (Table I.), a set of internal control potentiometers can be used to readjust EM61 gain. We recommend that the adjustment is done only if the deviation from the standard values is between ± 5 to ± 20%. For units that QC reading is outside 20% contact Geonics. Calibration adjustment should be performed only by a qualified technician.

6.1 Gain Adjustment Procedure

To get access to the Gain control potentiometers remove the electronic console from the backpack and proceed as per instructions on Figure 4. The Gain of the main (bottom) coil is adjusted by Trimmer R54, and the top coil Gain by Trimmer R23.

SKETCH OF EXTERNAL QC COIL

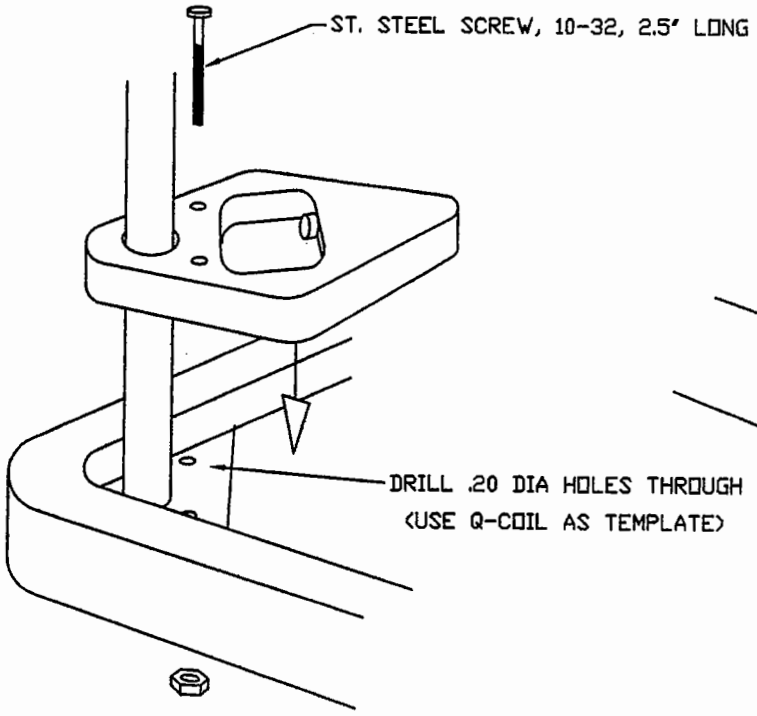


FIG 3a

SKETCH OF INTERNAL QC COIL

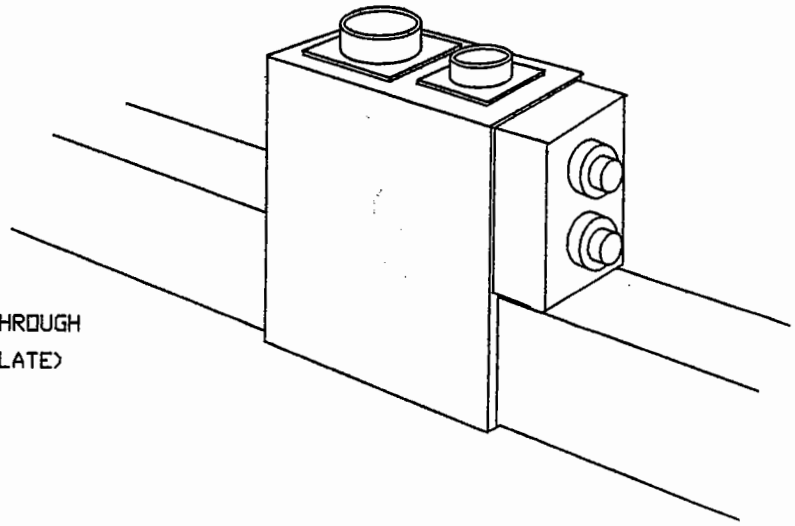
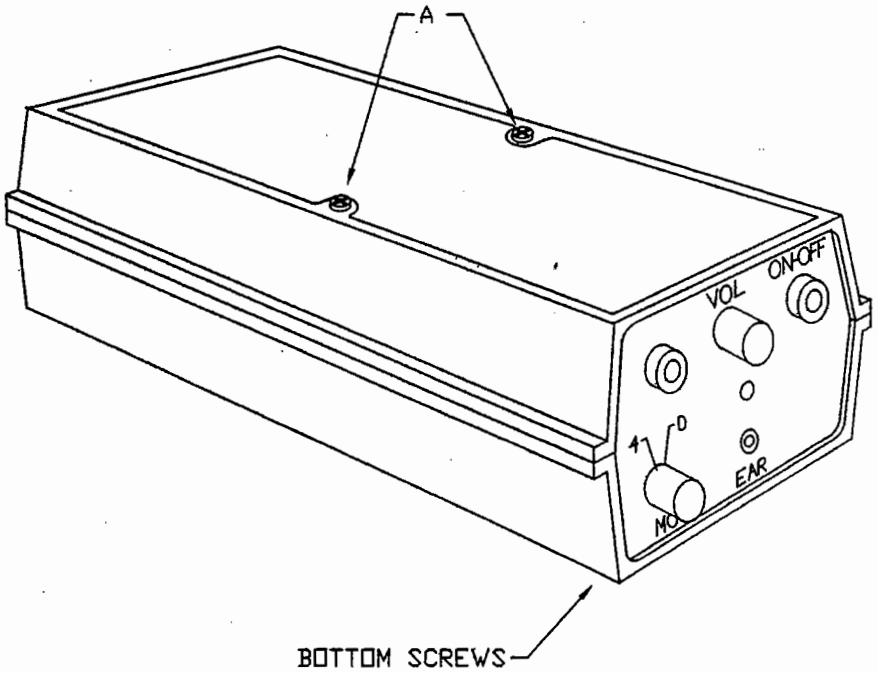
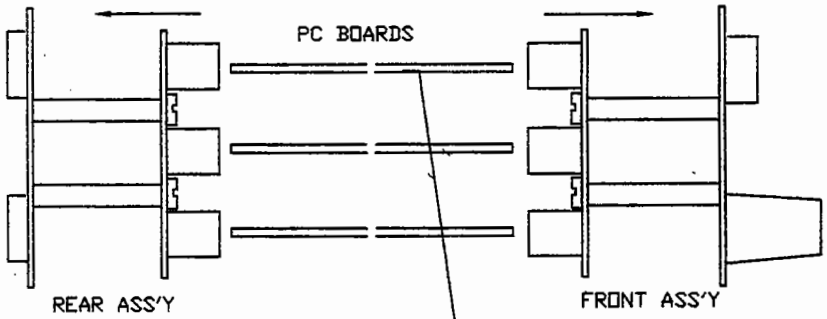
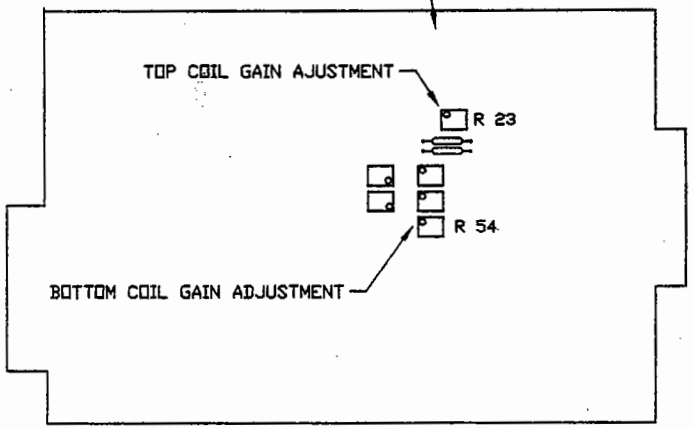


FIG 3b

EM61-MK2 RECALIBRATION







- REMOVE TWO SCREWS-A
- REMOVE FOUR BOTTOM SCREWS
- LIFT THE TOP COVER
- MAKE AJUSTMENTS ON TOP EXPOSED PCB
- ASSEMBLY THE UNIT IN REVERSE ORDER

FIG 4

The following table (Table II) gives the standard values for EM61-MK2HP units. Note that only the external QC Coil can be used. A special QC coil mounting support frame as shown in Figure 5, has been used.

7.1 Calibration Procedure

The calibration check procedure is as follows:

The instrument under test should be placed outdoors as for normal operation far from any larger metallic object. After the instrument nulling, the red button on the calibration device that is mounted as per Figure 5., should be pressed and held for about three to five seconds. The logger program or comparison with the standard table (Table II) will determine if the unit is operating properly. We suggest that ± 5% deviation from the standard value is considered acceptable.

7.2 Table II of the Standard Value

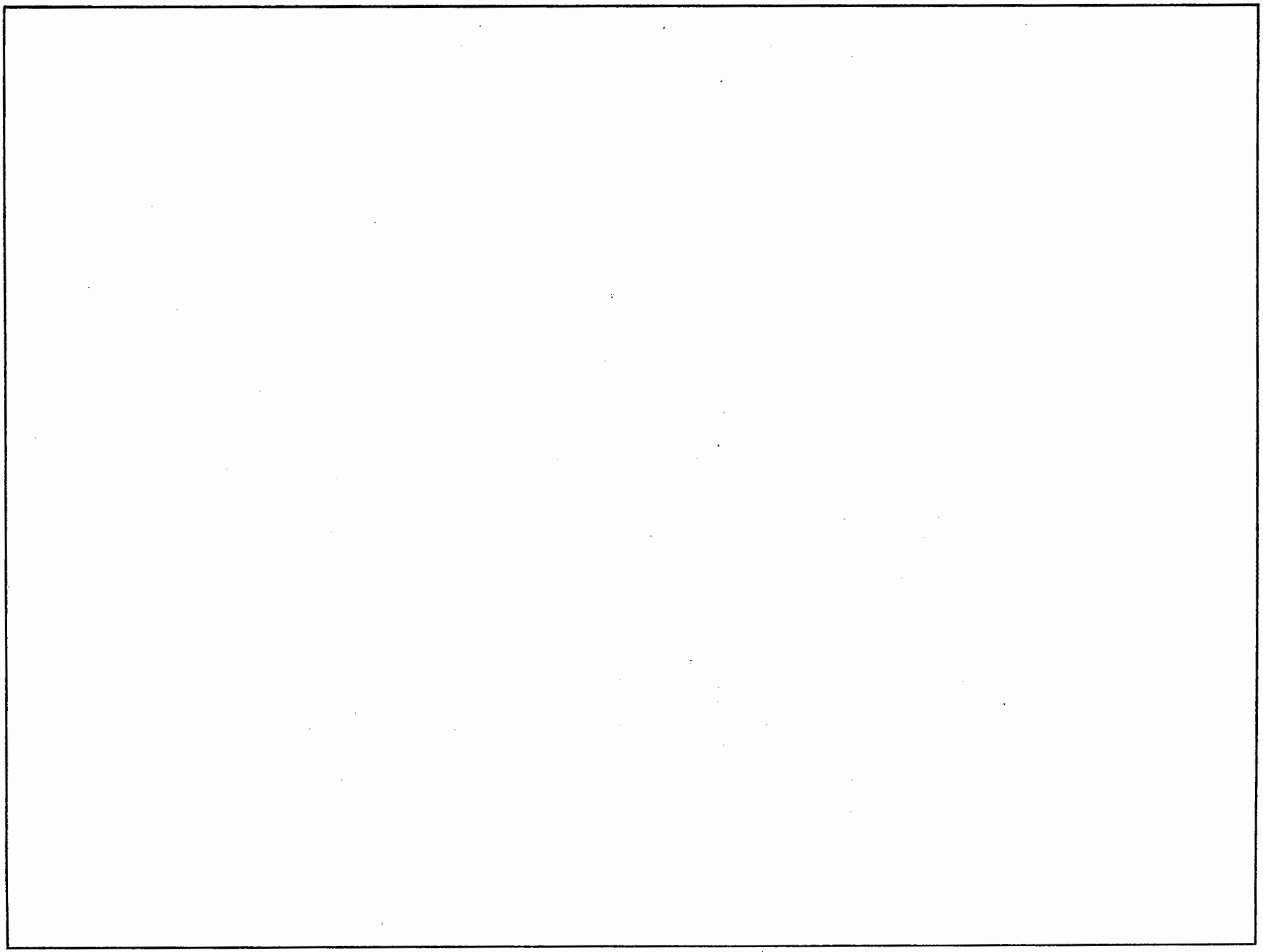
1. EM61-MK2 with 1 x 0.5 m Coil

A. External QC Coil

	Hi Power	Low Power
CH 1	- 2400 mV	- 1130 mV
CH 2	- 2010 mV	- 940 mV
CH 3	- 1560 mV	- 730 mV
CH 4	- 1120 mV	- 540 mV
CH T	- 1690 mV	- 810 mV

7.3 External QC Mounting

Figure 5 shows the position of the external QC coil mounted on a special QC coil frame that can be purchased from Geonics Limited. The QC coil has to be positioned in the middle of the support frame that is slightly off from the center of the bottom EM61-MK2HP coils.



EM61-MK2HP

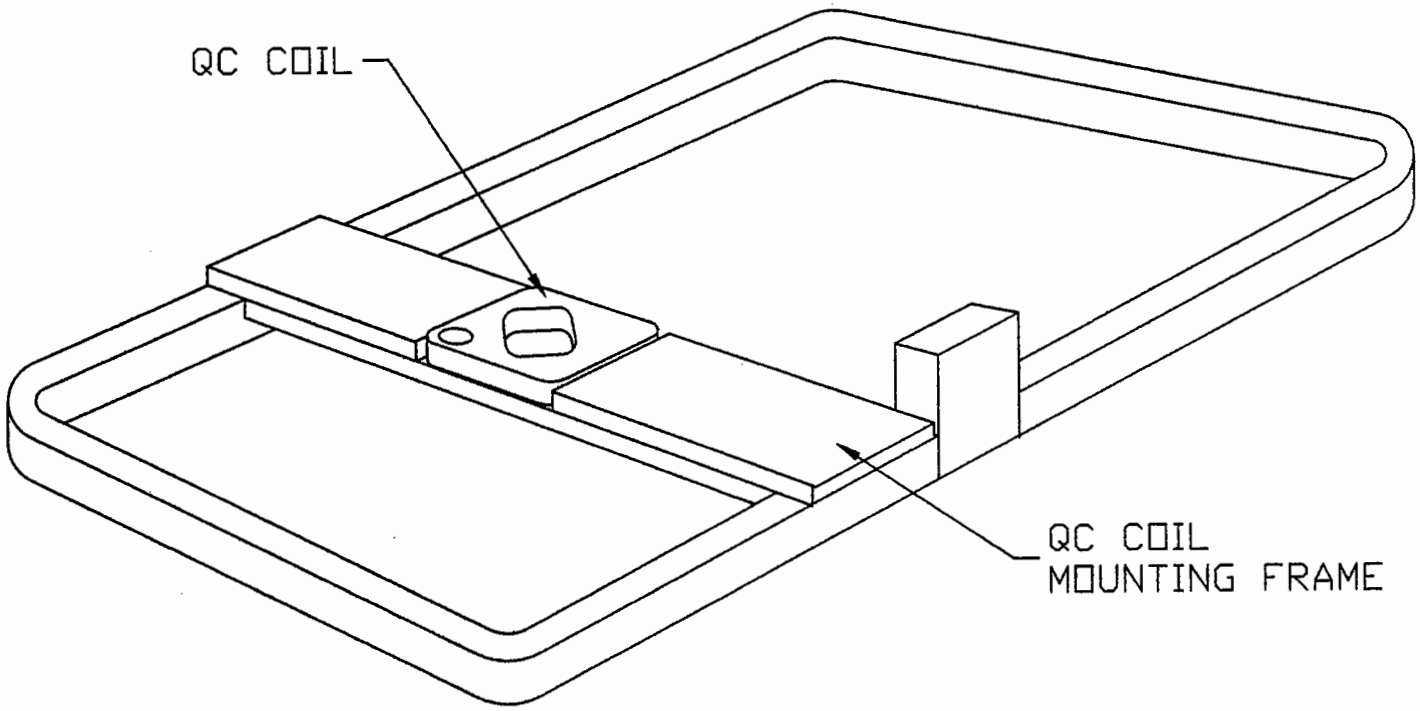


FIG 5

B. EM61-MK2 DATA LOGGING SYSTEM

OPERATING INSTRUCTIONS

EM61MK2 DATA LOGGING SYSTEM
FOR FIELD COMPUTER Allegro CX Field PC

EM61MK2

Version 1.02

July, 2005

Geonics Limited

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Tel: (905) 670 9580 Fax: (905) 670 9204

E-mail: geonics@geonics.com

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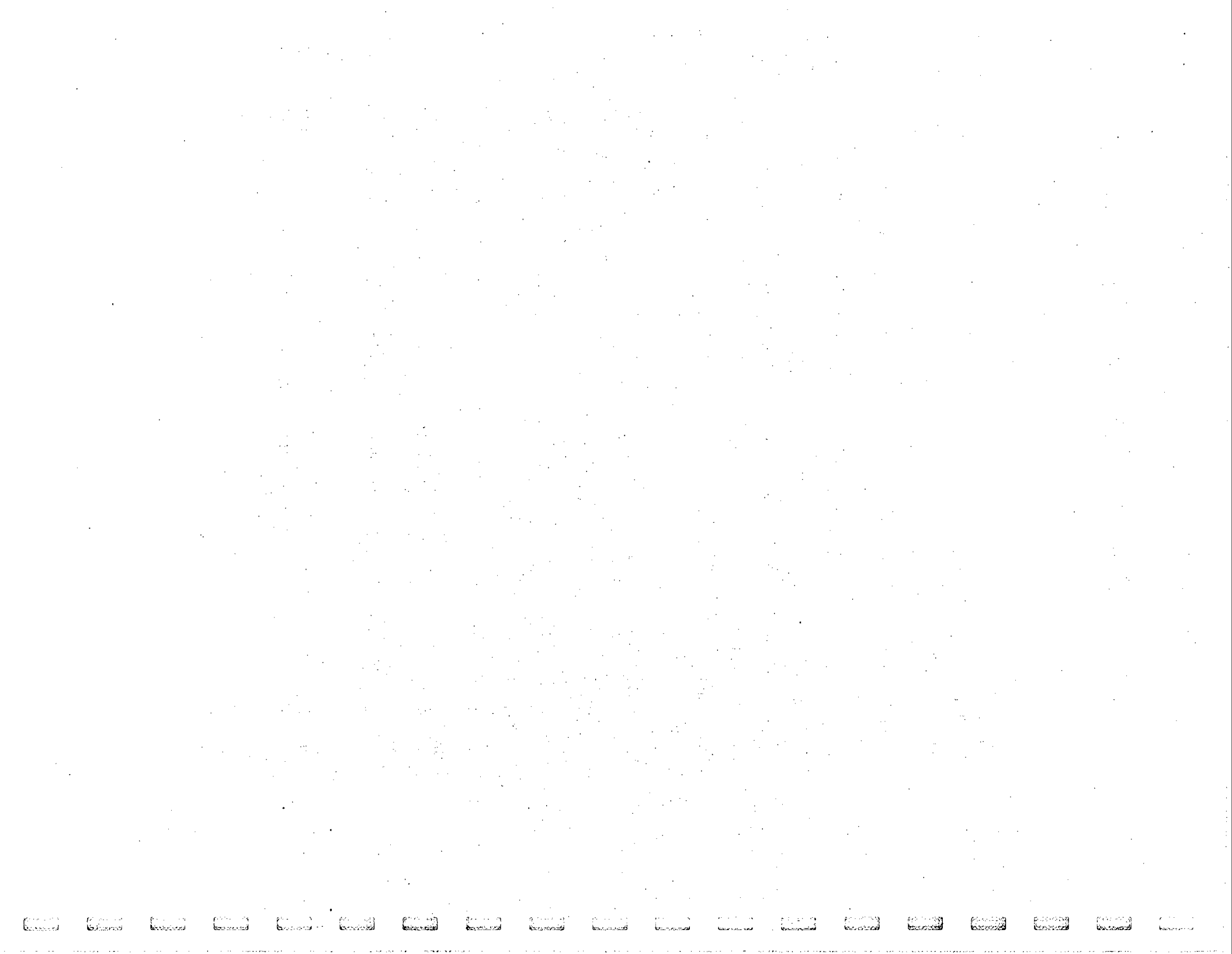


1. Introduction

The Geonics EM61MK2 Data Logging System (DAS70-CX) consists of a field computer Allegro CX, data logging program EM61MK2, and associated cable to connect the Allegro CX to the Geonics EM61-MK2 instrument. The program EM61MK2 is designed for the Allegro CX field computer and its MS Windows CE.NET V4.2 operating system.

The EM61MK2 program acquires and records survey data from the EM61-MK2 system, under the control of the operator. It also records various field information such as survey line number (line name), starting station, increment, comments, etc. Readings are displayed in graphic and text mode. Readings are displayed in real time in mV. In addition, the program allows you to monitor the instrument output while data is not recorded. The EM61MK2 program continuously monitors the condition of the instrument battery, without leaving the program. The EM61MK2 also provides the possibility of automatic nulling of the instrument output at any time during the survey.

The program allows the user to set the EM61-MK2 into a specific instrument mode of operation: AUTO, Wheel, or Manual modes. In AUTO mode readings can be automatically recorded in desired time intervals. In WHEEL mode readings are triggered by a counter installed at the EM61-MK2 wheel assembly, and in MANUAL mode readings are triggered manually by the operator.

The program supports the standard EM61-MK2 instrument as well as EM61-MK2 High Power unit. The program allows you to record data while using various EM61-MK2 antenna (1 x 0.5 m, 1 x 1 m, or 0.5 x 0.5 m sensors) and Geonics EM61HH-MK2 Hand Held sensor.

The EM61MK2 will accept NMEA-0183 compatible data from a GPS receiver directly connected to an Allegro field computer. GPS data which are embedded in the EM61MK2 data file can be processed later in the Geonics DAT61MK2 program. The connected GPS must be able to stream NMEA-0183 compatible messages. The EM61MK2 uses two NMEA messages GGA and GSA. While message GGA is mandatory, the GSA string is used only to provide information related to the GPS signal quality during data collection.

The EM61MK2 program records data together with a time stamp at each station. Data files created with this program can be used to position a survey according to locations recorded separately by a Global Positioning System (GPS).

Survey setup parameters are saved in a file, therefore they can be automatically used during subsequent data collection sessions.

The program has an option that allows you to view data files. Data files are saved to the programs current data directory by default. Data file names, which can be set by the program based on the computer clock or user specified, have extension names R61. Files can be transferred to a PC computer using a memory card, or by a serial or USB port using the MS ActiveSync program.

Over 1,000,000 readings can be collected in the Allegro field computer with a standard memory of 64 Mb. The maximum speed of data collection is approximately 16 readings per second assuming 1 Hz (or less) GPS input. In graphic display mode, a profile containing the last 150 data readings is displayed for each channel.

1.1 Program Requirements

To successfully use this software, you will need :

Computer

Field computer Allegro CX

Installed MS ActiveSync software (Version 3.50 or later) in desktop PC, or alternatively PCMCIA memory card to transfer files.

Geonics EM61-MK2

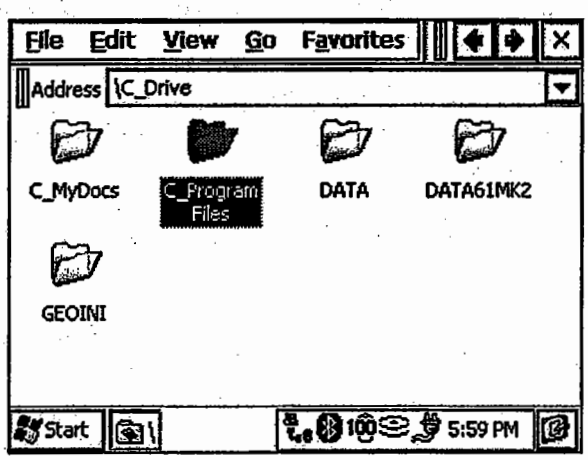
The EM61-MK2 instrument with associated cables.

The EM61MK2 program for Allegro CX is stored on DAT61MK2 CD disk. All necessary initial files (with extension names .INI) as well as data folder (DATA61MK2) are created in your field computer after the program is run for the first time. Check that the file EM61MK2.EXE is included in AllegroCX directory on the CD disk.

1.2 Installing EM61MK2

While using the Allegro CX the EM61MK2.exe file should be transferred from a desktop PC using MS ActiveSync software and USB or serial cable provided by manufacturer. Optionally the program can be transferred to an Allegro using the PC memory card.

It is recommended that the program be placed in non-volatile solid state storage. This memory is represented in the Allegro by the C_Drive icon. In the My Computer on the Allegro, double-tap on C_Drive icon, then folder C_Program Files will appear. The EM61MK2 program can be placed in C_Program Files. Folders for data files should be also created in C_Drive, which is a safe area to store data. The program creates folder DATA61MK2 which is the default folder for EM61-MK2 files.



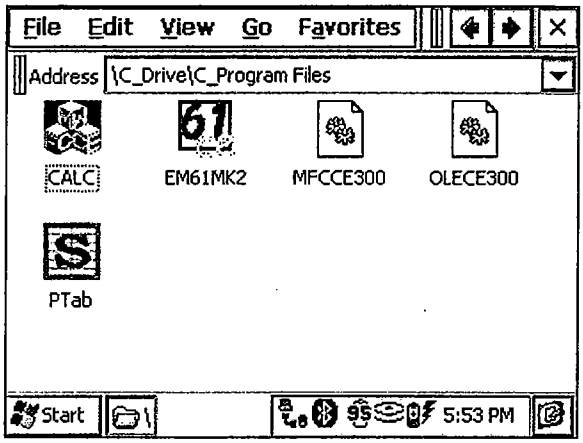
For more information about data storage options, refer to Chapter 3 of the Allegro CX manual.

1.3 Data Files Transfer

Data files are saved in the Allegro with extension R61. Transfer of files to desktop PC can be performed with MS ActiveSync or by PC memory card. Data files with extension R61 are binary raw data files. These files have to be converted to DAT61MK2 format with extension M61 (option "Convert Files" in DAT61MK2). Then they can be loaded and processed in the DAT61MK2 program.

1.4 Running EM61MK2 Program

To run the EM61MK2 locate program in C_Program Files and double-tap program icon. The EM61MK2 is a Windows CE based, button and dialog driven program designed to be simple to use. Although the program fully supports touchscreen interface, the keyboard entry may be more convenient in most field applications. The EM61MK2 can be fully operated from the keyboard when touchscreen functions are disabled by the user.

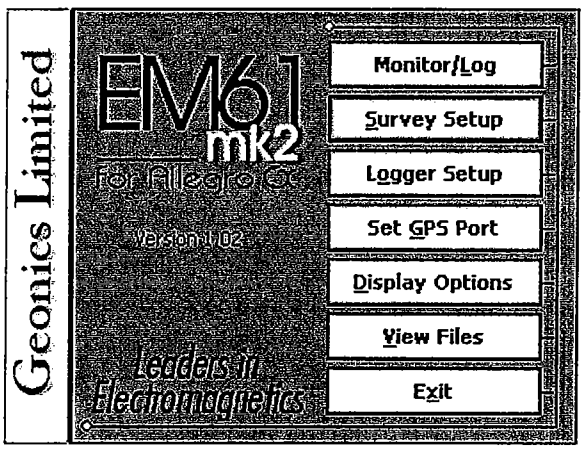


Options represented by the command buttons can be accessed by a single tap on the button. Buttons can also be selected from the keyboard by using shortcuts (pressing key corresponding to underline letter in button caption or by selecting button by pressing **TAB** and then execute by pressing **ENTER**. Shortcuts are the fastest way of accessing options represented by buttons.

Most options in the dialog windows are given in the form of text boxes and drop-down boxes which can be accessed using touchscreen or by the keyboard. Each dialog window has a title bar with a caption describing the dialog function and two buttons **OK** and **X (Cancel)**. The **OK** button (or key **ENTER**) confirms dialog selection. Tapping on the **Cancel** button (or pressing **Esc** key) closes the dialog and returns to the initial selection.

1.5 Main Screen

The Main Screen always appears after the program is started. It contains the name of the program, its version number, and a list of buttons representing the available options. The EM61MK2 Main Screen is displayed below.



These options are selected by using tapping buttons, or from keyboard using TAB/ENTER or shortcuts indicated by underline label characters. In case of Main Screen buttons the Down and Up arrow keys and <ENTER> can be used as well.

Short description for each of the options follows.

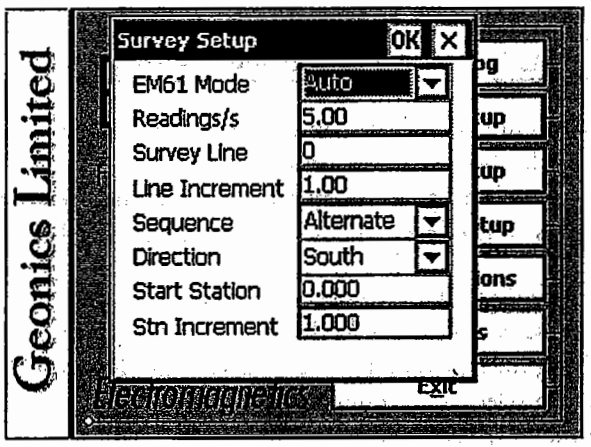
Short description of Main Screen options

Monitor/Log

This option allows to monitor and log the EM61-MK2 output. Monitor/Log screen starts always in Monitor mode, and then after a data file is created Logging mode is available. Monitor mode provides several options: the instrument nulling, performing Internal and External QC coil calibration, monitoring EM61-MK2 and Allegro battery level, etc.

Survey Setup

The Survey Setup dialog will be displayed. All survey settings (survey line name, increments, etc.) can be specified in this dialog.



Logger Setup

Dialog window that is associated with this option is used to set the instrument type, antenna size, serial port number, and type of pause key.

Set GPS Port

The GPS Port Setup dialog allows to disable and enable GPS data acquisition. This option is also used to set the serial port number used for GPS input and to specify necessary serial port communication settings. GPS monitoring window can be accessed from this dialog as well.

Display Options

The dialog which will allow you to specify colour and thickness of profile lines will appear. This dialog provides also choice of linear or compressed amplitude used for profile display.

View Files

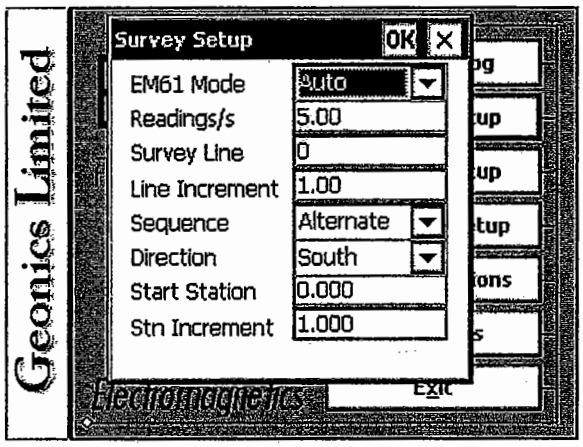
This option allows to review data files saved in Allegro.

Exit

This option will terminate the program execution.

2. Survey Setup

The Survey Setup dialog, presented below, contains several parameters which affect two important procedures: instrument settings (instrument mode, frequency of data collection, etc.) and survey geometry layout (survey line names, line spacing, start station, station increment, etc.).



Description of Options and Parameters:

EM61 Mode

This option allows you to select the type of instrument used. In the drop-down list box select Standard for the EM61-MK2 or High Power if EM61-MK2 High Power (HP) modification is used.

Set the EM61-MK2 mode of operation by selecting an item from the drop-down listbox labeled EM61 Mode. Available modes are: Auto, Wheel, and Manual. These modes of operation are described below.

Auto Mode

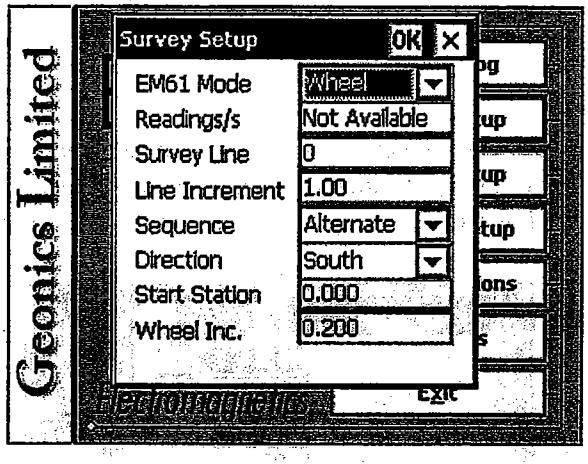
Readings will be triggered automatically at a specified frequency (see option Readings/s).

Please note that while in the former data acquisition system (DAS70) Stn Increment (station increment) had only two options: Positive or Negative, in the current program this value is optional.

Wheel Mode

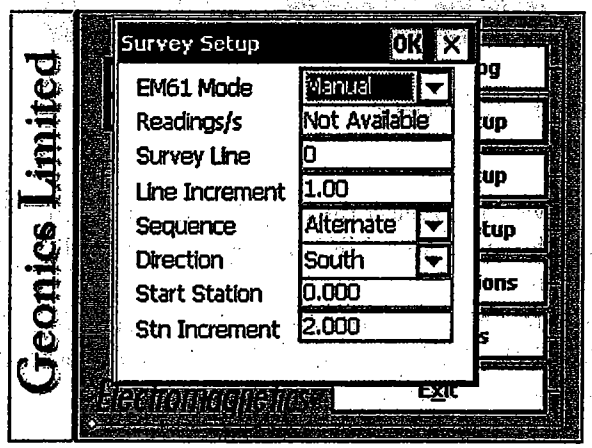
Readings will be triggered automatically by a counter attached to the wheel. Wheel increment is approximately 20 cm (or 0.64 foot) for the EM61-MK2 equipped with 1 x 0.5 m or 1 x 1 m antennas. The Hand Held EM61HH-MK2 has two wheel increments 0.1 and 0.2 m. Check the wheel increment setting on the antenna assembly.

When Wheel mode is selected option Reading/s is not available, see figure below. Please note that while in former data acquisition system (DAS70) Stn Increment (station increment) had only two options: Positive or Negative, in the current program this parameter is optional and its value has to be entered according to used wheel increment.



Manual Mode

Readings will be taken only while the manual trigger (switch on the logger cable) is pressed. This mode may be used only in very specific applications since the highly dynamic EM61-MK2 response requires finely spaced data points.
Please note that when Manual mode is selected option is not available.



Readings/s

When this option is available (only in Auto mode) activate text box by tapping or using TAB key and then enter desired value.

This parameter describes number of readings per second that will be taken. Any number larger than zero can be entered, however the EM61-MK2 maximum frequency of data output is 16 readings per second.

Survey Line (survey line name)

Activate text box by tapping or using TAB key and then enter desired name (number) for the survey line.

This is a user's tag number/name for the profile line. The length of the name can not exceed 8 characters. The line name is usually used as a coordinate perpendicular to the survey lines direction. For example, when survey lines are laid out along W-E direction stations describe W-E coordinate, while Line names may describe S-N (vertical on a map) coordinate.

Line Incr. (survey line name)

Activate text box by tapping or using TAB key and then enter desired for the survey line increment.

This parameter specifies the distance by which survey lines will be separated. This setting will be used to determine number (name) of the next survey line.

Sequence

Tapping on the down arrow next to the text box opens a drop-down box showing the available settings, or when the keybord is used activate the text box and then by using up or down arrow keys select one of two available items: Alternate and One Way.

Alternate is used when neighboring lines are surveyed in the opposite direction, which is the most common procedure during field surveys.

One Way is used when each survey line is traversed in the same direction.

The choice of this parameter will affect the default start station, a signature of the station increment, and line direction when parameters for the next survey lines is determined.

Direction

Tapping on the down arrow next to the text box opens a drop-down box showing the available options, or when the keyboard is used activate the text box and then by using up or down arrow keys select one of four available settings: East, West, South, and North.

This parameter indicates the heading of the survey line.

Start Station (start station of a survey line)

Activate text box by tapping or using **TAB** key and then enter the desired value for the start station.

This parameter specifies the starting station number for the selected survey line. This value is used in conjunction with Station Increment to calculate the current station number for display purposes.

Stn Increment (station increment)

Activate text box by tapping or using **TAB** key and then enter the desired value for the station increment.

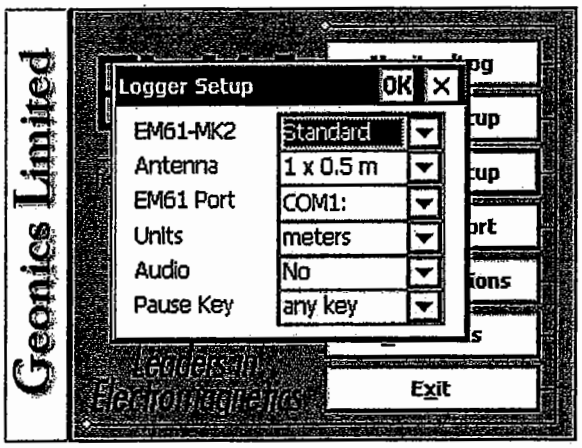
This parameter specifies the station increment for the selected survey line. This value is used in conjunction with Start Station to calculate the current station number for display purposes.

After all the parameters in the Survey Setup dialog are updated tap the button **OK** or press **ENTER** key to accept the displayed settings. The program will return to the Main Screen. Updated settings will be written to the initial file and they will be given as default parameters in the subsequent Survey Setup dialog.

To return to original settings (state before this dialog was selected) tap **Cancel** (X) button or press **Esc** key. All parameters will be reset to initial settings and the program will return to the Main Screen.

3. Logger Setup

This option allows you to specify used type of the instrument, antenna size and set several parameters in the logger. The Logger Setup dialog is presented below.



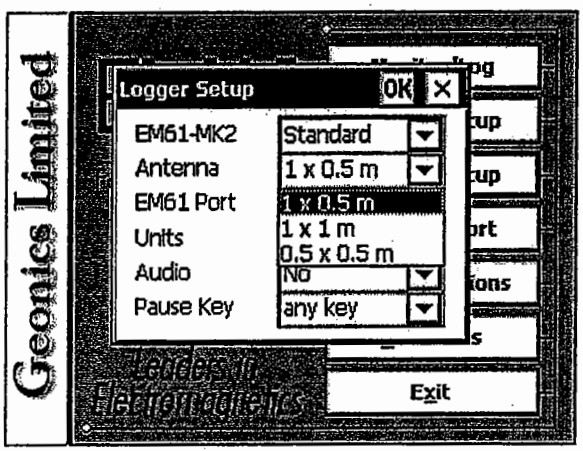
Description of Parameters:

EM61-MK2

This option allows you to select type of used instrument. In the drop-down list box select Standard for the EM61-MK2 or High Power if EM61-MK2 High Power (HP) modification is used.

Antenna

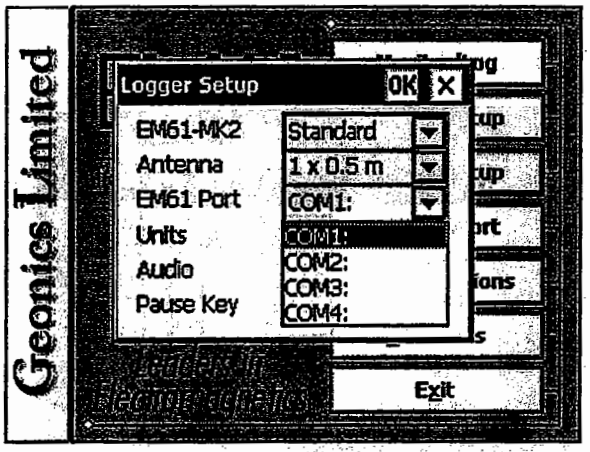
The Antenna option allows you to select the size of the EM61-MK2 sensor. If the EM61HH-MK2 Hand Held antenna is used this option can be ignored. If the standard antennas are used (1 x 0.5 m, 1 x 1 m, or 0.5 x 0.5 m) the size of the sensor must be specified before monitoring the instrument output. Select proper size of the EM61-MK2 sensor in the drop-down list box labeled Antenna.



EM61 Port

The number of serial port that is assigned to the EM61-MK2. Available selections: COM1, COM2, COM3, and COM4. The program default is COM1. Communication parameters for the selected serial port are set by the program, since the EM61-MK2 operates at fixed settings: Baud Rate (9600), Parity (N), Data Bits (8), and Bit Stop (1).

This port must be different than the port specified in the Set Port for GPS option (see chapter), otherwise a message will be displayed and ports will have to be reassigned.
Select port number in the drop-down list box (see Figure below).



Units

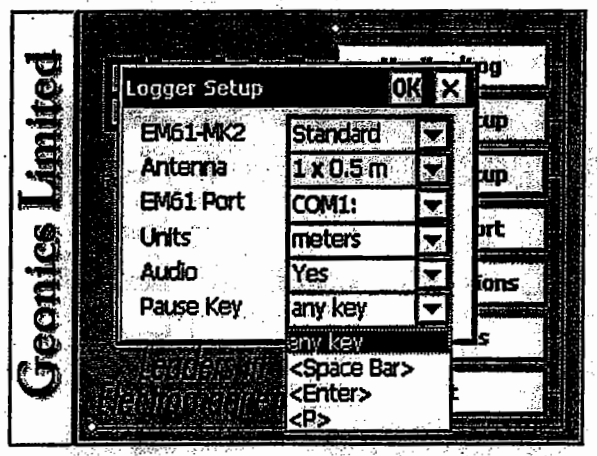
Two selections are available: **Meters** or **Feet.**

Audio

Two selections are available: **Yes** or **No.** The audible click will be generated at each reading when this option is enabled. At fast rate (above 5 readings/s) the sound may appear not uniform, however this does not affect quality of data acquisition.

Pause key

Four selections are available: **any key, Space Bar, Enter,** and **P** This feature is used to pause data recording during logging session. Default setting **any key** can be changed to one of the three specific keys for field conditions where a logger key can be accidentally pushed causing unwanted stop of data logging.

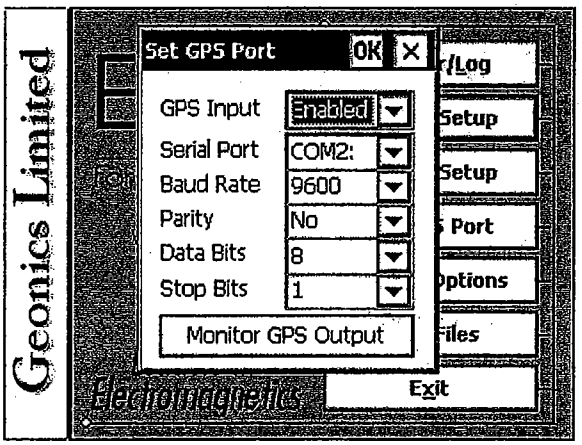


After all the parameters in the Logger Setup dialog are updated tap the button **OK** or press **ENTER** key to accept the displayed settings. The program will return to the Main Screen. Updated settings will be written to the initial file and they will be given as default parameters in the subsequent Logger Setup dialog.

To return to original settings (state before this dialog was selected) tap **Cancel** (X) button or press **Esc** key. All parameters will be reset to initial settings and the program will return to the Main Screen.

4. Set Port for GPS

After the Set Port for GPS button was tapped (or executed from the keyboard) in the Main Screen the Set Port for GPS dialog window appears on the screen. This dialog allows you to enable and disable the GPS input, specify serial communication parameters matching GPS receiver settings, and to monitor the GPS output in terminal mode (the bottom button). The dialog is presented below.



Description of Options and Parameters:

GPS Input

This option allows you to Enable/Disable a serial port for GPS input. When Disabled is chosen logging and monitoring screens will display message "GPS disabled" in place of GPS parameters.

The GPS Input can be Enabled even if there is no GPS system connected to the Allegro. In such case data file will contain proper sequence of EM61-MK2 readings without any GPS input.

Tapping on the down arrow next to the text box labeled GPS Input opens a drop-down box showing the available settings, or when the keyboard is used activate the text box by pressing TAB key and then by using up or down arrow keys select one of two available items: Enable and Disable.

Serial Port

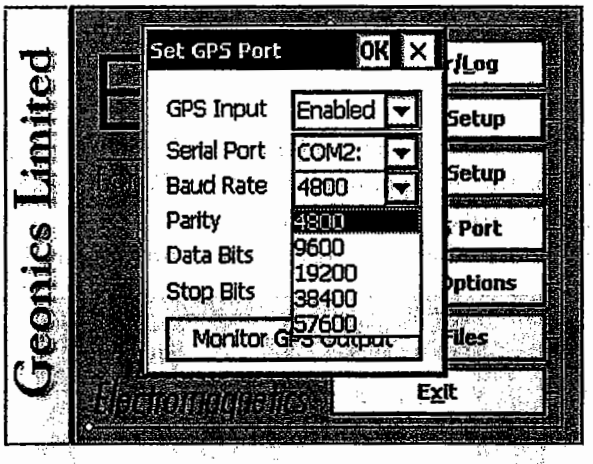
The number of serial port that is assigned to the GPS input. Available selections: COM1, COM2, COM3, and COM4. The program default is COM2. Communication parameters for the selected serial port can be determined in options described below.

This port must be different than the port specified in the Logger Set Up menu (for EM61-MK2), otherwise a message will be displayed and ports will have to be reassigned.

Tapping on the down arrow next to the text box labeled Serial Port opens a drop-down box showing the available ports, or when the keyboard is used activate the text box by pressing TAB key and then by using up or down arrow keys select one of available items.

Baud Rate

Specify Baud Rate for the output port, the selected value should match the Baud Rate of the GPS system, default is 9600. Available settings are: 4800, 9600, 19200, 38400, 57600, and 115200.



Tapping on the down arrow next to the text box labeled Baud Rate opens a drop-down box showing the available parameters, or when the keyboard is used activate this text box by pressing TAB key and then by using up or down arrow keys select one of available items.

Parity

Select Parity for the output port, the parameter should much the Parity set in the GPS serial port settings. Available settings are None, Even, and Odd; default is N.

Tapping on the down arrow next to the text box labeled Parity opens a drop-down box showing the available parameters, or when the keyboard is used activate this text box by pressing TAB key and then by using up or down arrow keys select one of available items.

Data Bits

Specify Data Bits for the output port, the selected value should much settings in the GPS receiver, default is 8. Other available selection is 7.

Tapping on the down arrow next to the text box labeled Data Bits opens a drop-down box showing the available parameters, or when the keyboard is used activate this text box by pressing TAB key and then by using up or down arrow keys select one of available items.

Stop Bits

Specify Stop Bits for the output port, the selected value should much settings in the GPS receiver, default is 1. Available selections are 1 or 2.

Tapping on the down arrow next to the text box labeled Stop Bits opens a drop-down box showing the available parameters, or when the keyboard is used activate this text box by pressing TAB key and then by using up or down arrow keys select one of available items.

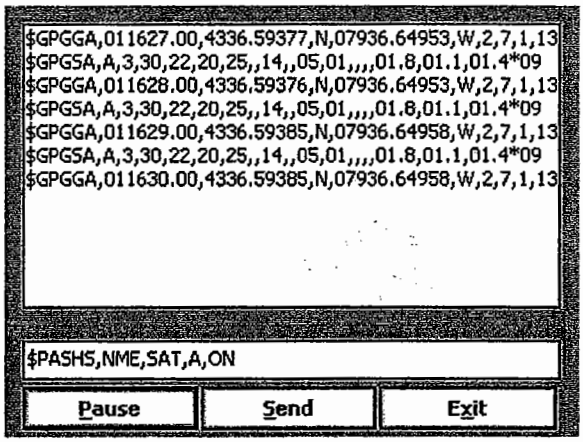
After all the parameters in the Set GPS Port dialog are updated tap the button **OK** or press **ENTER** key to accept the displayed settings. The program will return to the Main Screen. Updated settings will be written to the initial file and they will be given as default parameters in the subsequent Survey Setup dialog.

To return to original settings (state before this dialog was selected) tap **Cancel** (X) button or press **Esc** key. All parameters will be reset to initial settings and the dialog window will disappear.

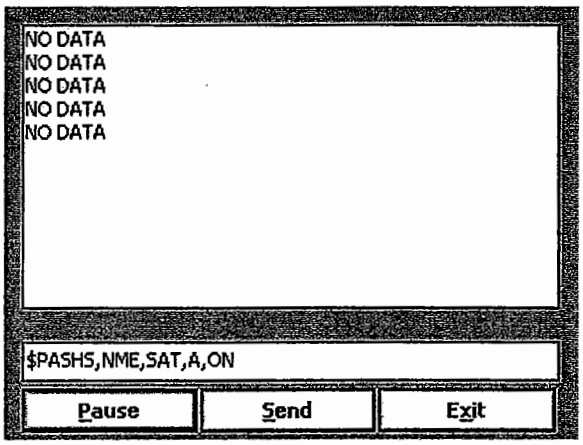
To activate terminal mode which allows you to monitor GPS receiver output tap the button labeled Monitor GPS Output, or when using keyboard select this button using **TAB** key and press **ENTER**. The monitoring mode will work regardless of the GPS Input being Enabled or Disabled. This option is described in the following section.

4.1 Monitoring GPS Receiver Output

After the button Monitor GPS Output is tapped or executed by the keyboard the program will display the screen in terminal mode. In this mode the screen is divided into three parts. The largest, top portion of the screen displays the GPS receiver output. The middle portion shows that last NMEA command sent to the GPS receiver (by default command shown in Figure below), and at the bottom three buttons representing available options: Pause/Go, Send, and Exit. These buttons can be tapped, executed by TAB key and ENTER keys, or by using shortcuts (pressing underlined letter keys). This screen is shown below.



As soon as the EM61MK2 screen is in terminal mode and the GPS is streaming data, each message transmitted by GPS receiver will appear in the top portion of the display (the end may be cut off if an NMEA message is longer than screen). The display is updated with the frequency the GPS receiver outputs data. This allows you to recognize the GPS update rate and type of messages being sent by the connected GPS. In cases where the GPS data is not received by the logger a message NO DATA and current time will appear in the top window of the display, as shown below.



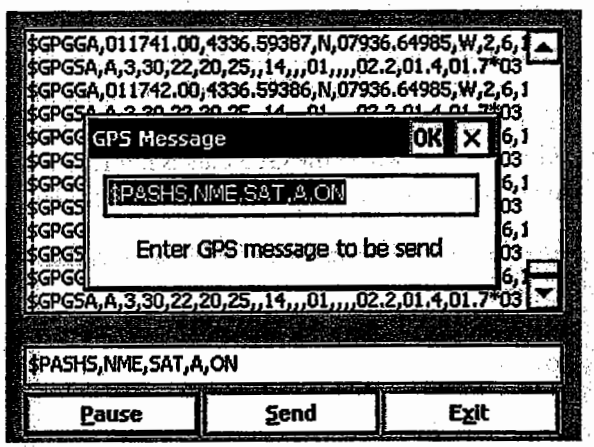
The message NO DATA is normally updated with a rate of 7 seconds. This may indicate the following: serial port number not correctly specified in Set Port for GPS dialog, GPS receiver not sending any data, and not working or not connected GPS receiver. If the message is updated more often than 7 seconds (i.e. every 1 or 2 seconds) or the display does not show legible characters, it is possible that the GPS is working correctly and is connected to the proper serial port, however communication parameters are not specified correctly. In most cases the Baud Rate or Parity must be adjusted.

The NO DATA message may also appear if the GPS data are received correctly, but the GPS receiver was set to send data with a time interval longer than 7 seconds. In this case the NO DATA message will be displayed in between GPS messages. This indicates that the GPS is working correctly, however the operator should consider adjustment of the GPS receiver output update rate. Most high resolution geophysical surveys require positioning update of 1 or 2 seconds, and a 5 seconds interval can be used only when the survey is carried out at an even pace and along relatively straight survey lines.

The monitoring display can be stopped any time by using button labeled **Pause**. At that time scrolling of the GPS output will be stopped, and the button will be labeled **Go**. The next tap (or keyboard action) on this button will activate receiving and display of GPS data.

The button labeled **Send** allows you to send a NMEA command to the GPS receiver. It is preferable if the GPS receiver parameters are set using the GPS manufacturer software or controller (GPS logger or panel keys). However, **when the operator is familiar with NMEA protocol and structure of commands for a given GPS system,** this function can be very convenient and useful when the update rate and enabling or disabling messages in the data stream is required.

After the button **Send** is tapped a dialog titled GPS Message is displayed and the beginning of the standard NMEA command, **$PASHS,** or the last entered command is displayed. After the entire NMEA command is typed in, tap **OK** button or press the key **<ENTER>** to send the command to the GPS receiver. Tapping **Cancel** button or pressing the **<Esc>** key will cancel the command and hide the NMEA Message dialog. An example of a command that will enable the NMEA message **SAT** is given in the below figure (it is assumed that the GPS receiver output serial port is A).

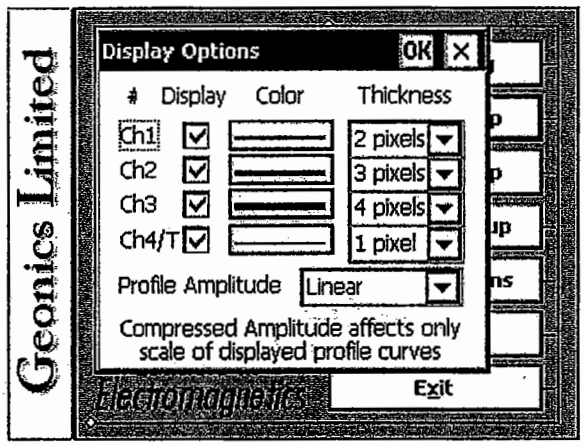


After this command is received by the GPS receiver, the confirmation message will be send by the receiver ($PASHR, ACK*3D) and data stream will contain the message SAT ($PASHR, SAT,..... in the above figure).

Please note, that not every GPS system accepts and uses the same standard set of NMEA commands and messages. In addition, some GPS systems do not accept commands sent by the serial port at all. The configuration of these type of receivers can be updated only by the controlling device (usually GPS logger, controller, or the receiver panel keys).

5. Display Options

After the **Display Options** button was tapped (or executed from the keyboard) in the Main Screen the Display Options dialog window appears on the screen. This dialog allows you to enable and disable the display of each channel profile, specify color and thickness of profiles, and select linear or compressed amplitude for profiles. The dialog is presented below.



Description of Options and Parameters:

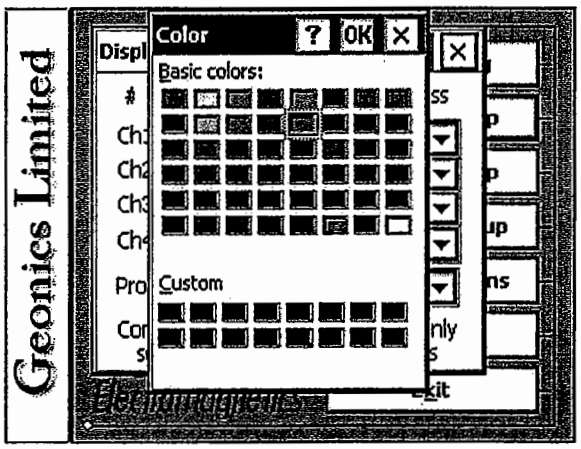
Display

To enable or disable displaying of each channel profile tap on the corresponding button labeled Display. Profiles of all channels with checked buttons will be displayed during data logging.

Regardless of which channels are chosen to be displayed as profiles, data for all four channels will be displayed in numeric form below profile display.

Color

To change colour of each profile tap the coresponding button (with colour line) labeled Color. The following dialog titled Color will appear.



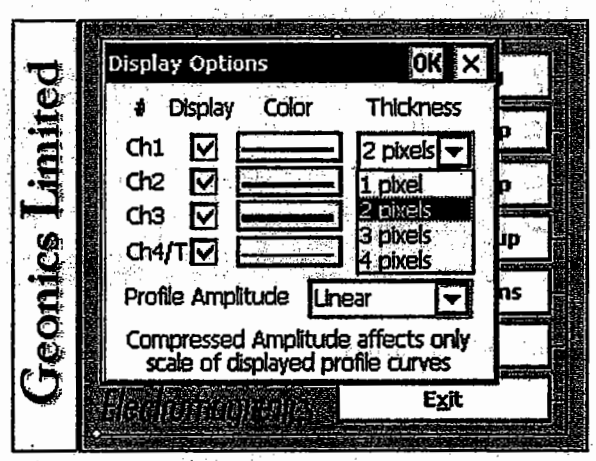
Select desired colour by tapping on a colour box (the selected colour box will be highlighted).

Tap the button **OK** or press **ENTER** key to accept the highlighted colour. The Color dialog will disappear and the colour of the appropriate channel button will updated. To cancel colour selection tap **Cancel** (X) button or press **Esc** key.

Thickness

Specify thickness of a profile for a desired channel by using one of four drop-down boxes labeled thickness. Thickness of a profile curve is expressed in pixels. Available settings are: 1, 2, 3, or 4 pixels.

Tapping on the down arrow next to the text box (labeled by number of pixels) opens a drop-down box showing available selection (see Figure below). Select thickness by tapping on the desired selection. If keyboard is used activate text box by pressing TAB key (till the box is highlighted) and then by using up or down arrow keys select one of available items.



Profile Amplitude

This option allows you to select Linear or Compressed amplitude scale for profiles. The compressed amplitude (squre root function) allows you to display the high dynamic range of the EM61-MK2 data in a legible way and it is recommended.

Tapping on the down arrow next to the text box labeled Profile Amplitude opens a drop-down box showing available parameters, or when keybord is used activate this text box by pressing TAB key and then by using up or down arrow keys select one of available items.

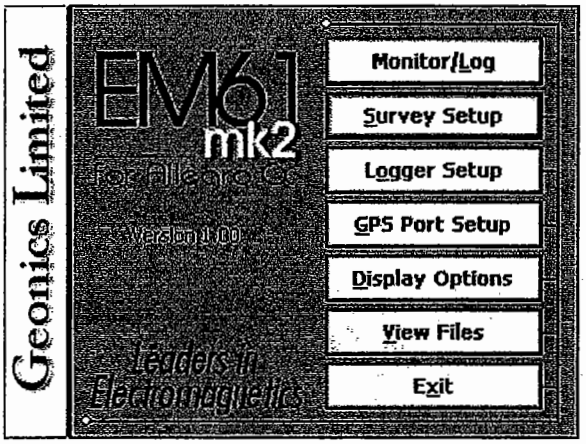
Please note, that readings in numeric form are always given in mV (linear scale) regardless of the Profile Amplitude selection. Further, graphic display in the compressed scale does not affect readings saved in the data file. Data are always written to file in original form.

After all the parameters in the Display Options dialog are updated tap button **OK** or press **ENTER** key to accept the displayed settings. The program will return to the Main Screen. Updated settings will be written to the initial file and they will be given as default parameters in the subsequent Survey Setup dialog.

To return to original settings (state before this dialog was selected) tap **Cancel** (X) button or press **Esc** key. All parameters will be reset to initial settings and the dialog window will disappear.

6. Logging Data

After the **Monitor/Log** button (in Main Screen) is tapped or executed by the keyboard, the program enters logging session which contains three modes: Monitoring, Stand By and Logging. Program starts logging session always in Monitoring mode. In this mode EM61-MK2 readings and GPS

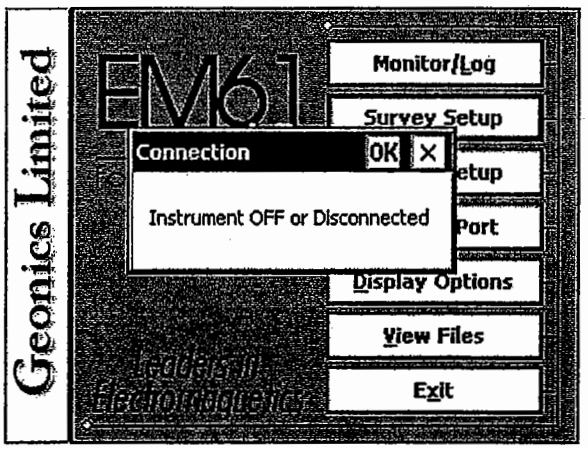


parameters can be quickly examined and some functions (creating data file, nuling, QC coil check) can be performed. After a data file is created in Monitoring mode, the program switches to Stand By mode and allows access to Logging mode. In Stand By mode instrument output can be monitored and some survey and logging parameters can be changed, and Logging mode is used only to record data. Two modes Stand By and Logging are toggled by **GO** and **Pause** buttons.

6.1 Monitoring Mode

The Monitor mode allows initial inspection of the range of the instrument readings at a particular site, monitoring the instrument performance, quick inspection of the condition of the instrument battery, perform QC Coil check, and setting zero level of the instrument.

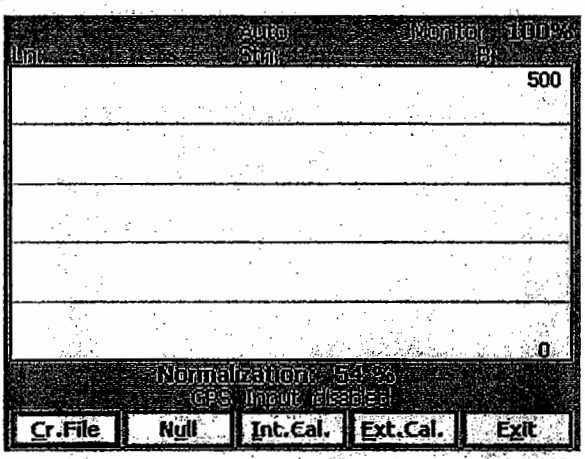
It is assumed that the instrument is turned ON prior to using this option. If the instrument is OFF or the instrument console is not connected to the computer the following message will appear:



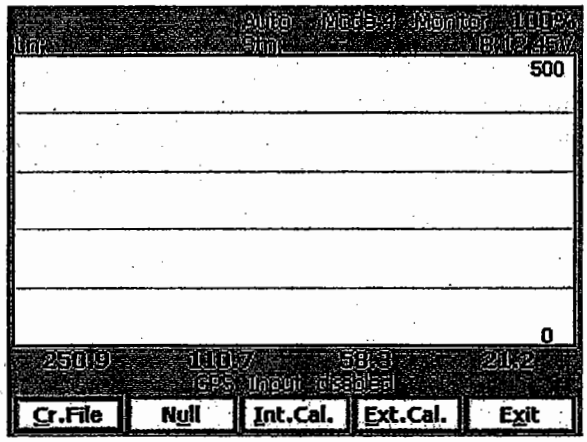
Check the connection or turn the instrument ON and select the Monitor/Log option again.

Assuming that the instrument works properly the program will display the Monitor mode window and will start normalization session which lasts less than 10 seconds. At this stage the Monitor window will display the following message:

After the normalization is finished the layout of the Monitor window is as follows:



The Monitor (as well as Stand by and Logging) window is divided into four sections.



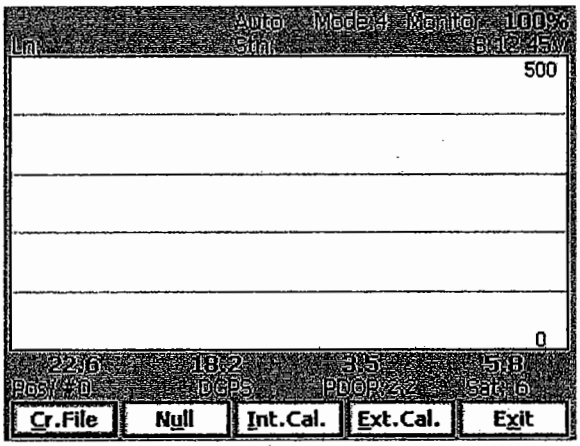
Two lines of text in the top section provides survey parameters (used in Stand By and Logging modes) and instrument information. In Monitor mode this section displays: instrument mode (4 or D), current display mode (Monitor, Stand By or Logging), Allegro battery level (in % of full charge), and the EM61-MK2 battery level in Volts (following label **B:**). When fiducial marker is pressed then **M** is displayed next to label **Stn:**.

The second, largest graphic section will be used to display profiles during logging data.

The third section contains two lines of text. The first line is used to display EM61-MK2 readings and the second line of text provides GPS related information.

If Mode 4 was selected on the instrument panel (it is displayed at the top of the screen) channels **1, 2, 3,** and **4** will be displayed under profile window, and when Mode D was selected (for Top and Bottom antennas) channels **1, 2, 3,** and **T** will be given in the Monitoring window. Channels are not labeled and they are displayed from the left in ascending order: 1, 2, 3, and 4, or 1, 2, 3, and T. The EM61-MK2 readings are updated approximately 10 times per second during the monitoring session.

When GPS was Disabled in the Set GPS Port dialog a message **GPS Input: disabled** will be displayed. If the GPS port is Enabled and a working GPS receiver is connected to the field computer the Monitoring screen will display GPS parameters, as presented below.



In the above Figure one line of the display is dedicated to show the GPS status. A label **Pos/#** will be used during data acquisition, it will provide the number of GPS positions saved in the data file. In Monitor mode this label indicates GPS activity by toggling between forward (/) and back (\) slash (that follows label **Pos**) every time the program receives a message from the GPS receiver. If the slash is not changing for long periods of time it means that the GPS receiver is not working or that it is not connected to the field computer. A label **DGPS** (Differential Global Positioning System) indicates that GPS readings are differentially corrected in real time, while label **AGPS** (Autonomous Global Positioning System) indicates lack of differential correction. The next label **PDOP** with a value varying between 0 and 99.9 represents an index called Position Dilution of Precision (**PDOP**). This value is available only when messages both, GGA and GSA are received from GPS. The last label **Sat** and following number shows number of currently tracked satellites. Refer to section 9 (Set Port for GPS), Appendix A, and to GPS manuals for more information about GPS parameters.

The fourth section of the Monitor window lists the program functions available directly in the Monitor mode given at the bottom of the screen in form of buttons. Available options are as follows: **Cr.File** - create data file, **Null** - Nulling, **Int.Cal.** - Internal QC-coil calibration, **Ext.Cal.** - External QC-coil calibration, **Exit** - exits the Monitor mode and returns program to Main Screen.

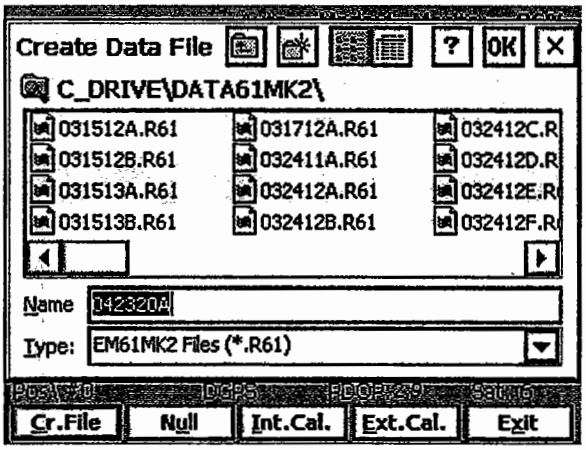
Description of Monitoring Mode Options

Cr.File *(create data file)*

When a data file is created the program will switch to Stand By mode automatically.

The log file can be created in the given default directory (DAT61MK2) or in any other directory in the Allegro CX. If other directories are used, please note that only subdirectories of C_Drive represent save, non volatile memory.

The name of the file is given by the field computer clock and it consists of month (2 digits), day (2 digits), hour (2 digits), and one alphabetic character A, B, C, etc. (If all letters during one hour are used use the Overwrite option). The Create Data File dialog is presented below.



The file name can be specified in the Create Data File dialog using the Windows standard interface procedure. The EM61-MK2 data files cannot be appended.

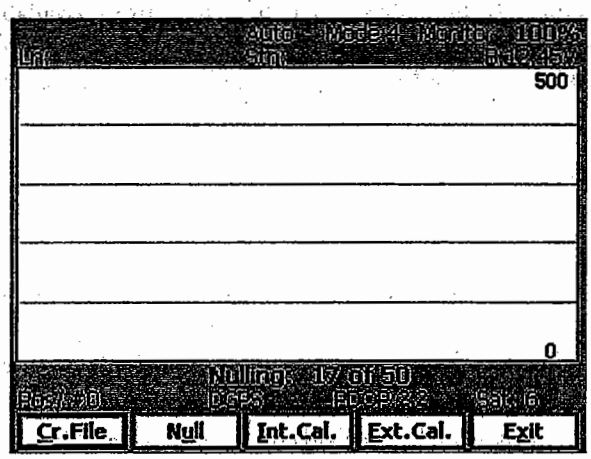
Each data file in the field computer (raw data file) has an extension name R61 and it is created in the directory specified in Create Data File dialog. The R61 files are created in the instrument binary format. They can be viewed using the Main Screen option "View Files". These files can be also converted to ASCII format and processed in the Geonics DAT61MK2 program.

After the file is specified tap the button **OK** or press **ENTER** key to accept and create data file. The program will switch Monitor mode to Stand By mode and the data file will be displayed on the screen.

To cancel selection and return to Monitoring mode tap the **Cancel** (X) button or press **Esc** key.

Null

To perform a null of the instrument tap the button labeled **Null** or execute this option using the keyboard (navigate to the button by pressing **TAB** key and when highlighted press **ENTER** key, or use shortcut - press key **U**). At this moment the computer takes 50 readings and calculates the instrument offset.

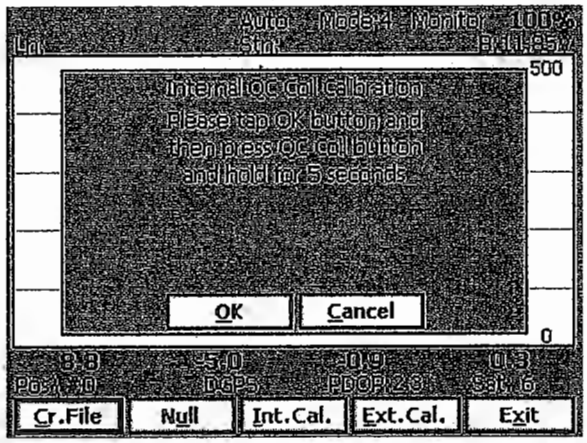


The calculated offset is applied to all the readings that follow this operation. If needed, this procedure can be repeated several times until satisfactory results are obtained. However, there is no associated "Undo" function. If original values (without calculated offsets) of the EM61-MK2 readings are needed, exit the EM61MK2 program and run it again. The EM61-MK2 instrument does not have to be turned OFF. Null operation can be also performed later during data collection.

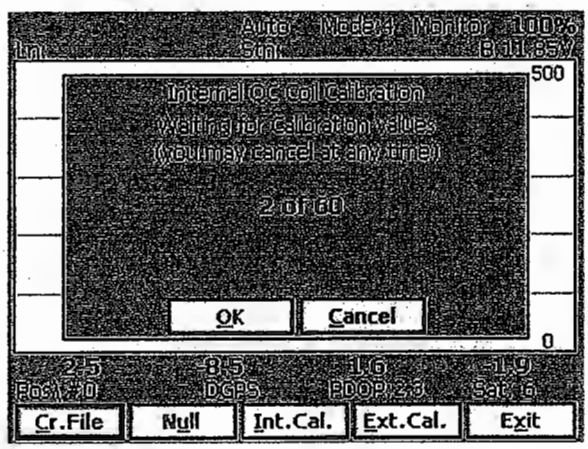
Int.Cal. *(Internal QC Coil Calibration)*

The Internal QC coil calibration is described in detail in the EM61-MK2 Operating Instructions.

To start the calibration using Internal QC coil tap the key labeled **Int.Cal.** or execute this option by keyboard (navigate to the button by pressing **TAB** key and when highlighted press **ENTER** key, or use shortcut - press key **I**). This action begins by performing the automatic nulling which in this case is only in effect for the duration of the calibration process. It will not affect EM61-MK2 readings. After the nulling is completed (less than 5 seconds) the Internal QC coil Calibration window is displayed.



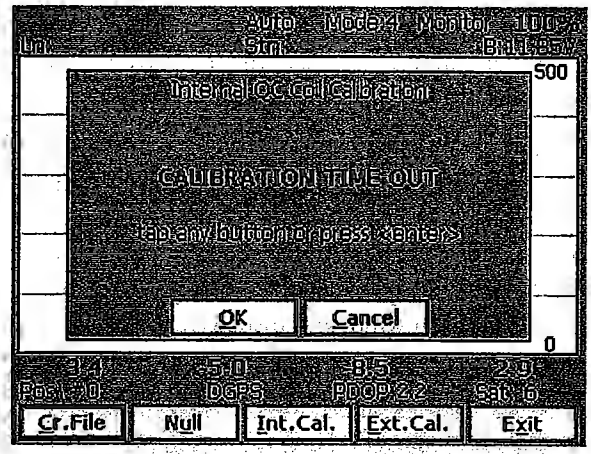
After **OK** button is tapped (or shortcut key **O** is pressed) the window displays timer with elapsed seconds and EM61-MK2 readings. This display lasts for 60 seconds. During this time please follow the instructions provided on the Allegro screen.



Internal QC coil calibration can end in the following four ways:

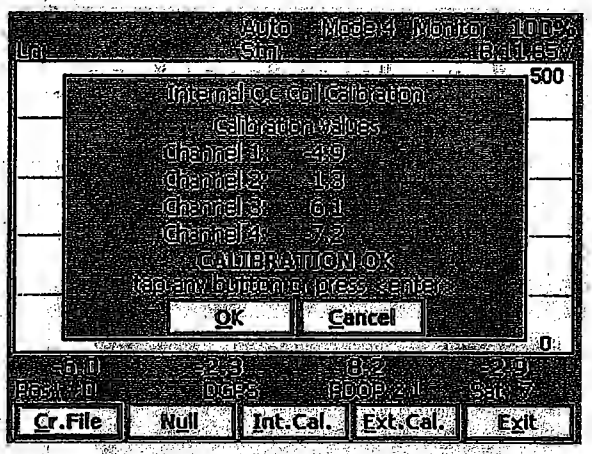
The process can be stopped by an operator at any time by tapping **Cancel** button or pressing shortcut key **C.**

The calibration may end by time out (60 seconds) if QC coil button was not pressed or this action did not activate QC coil. The following screen will then be displayed:

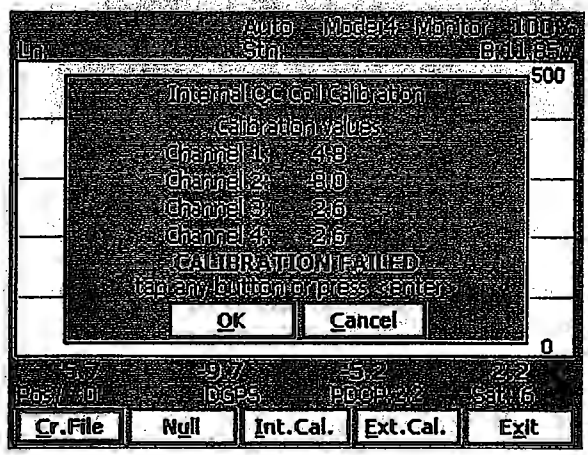


After pressing any key the program returns to Monitoring window. To repeat Internal QC coil calibration please tap the **Int.Cal.** button again.

The logger will determine if the instrument has passed test. If after activating the QC coil, the program determines that the reading is inside the standard values within +/- 10% tolerances then a message "CALIBRATION OK" will be displayed (see below).



Otherwise, if the program determines that the reading is outside of the test values range the corresponding message "CALIBRATION FAILED" is displayed.

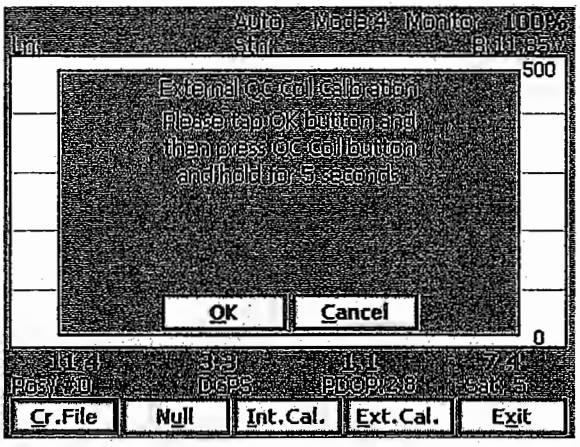


Regardless of the test result (OK or FAILED) the readings will be saved on screen. The program returns to Monitoring window after any button is tapped or ENTER key is pressed. Then the Internal QC coil calibration process can be repeated.

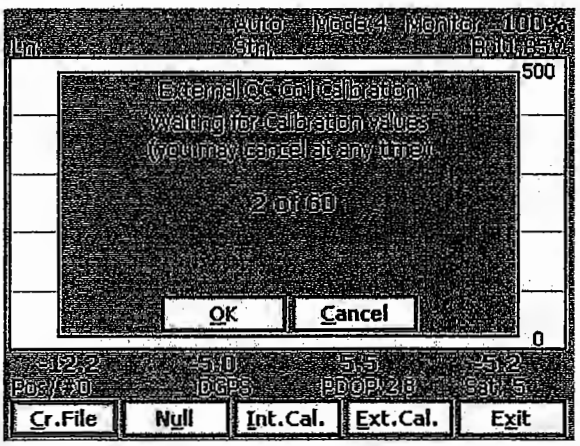
External QC Coil Calibration

The External QC coil calibration is described in detail in the EM61-MK2 Operating Instructions.

To start the calibration using the Internal QC coil tap the button labeled **Ext.Cal.** or execute this option by keyboard (navigate to the button by pressing **TAB** key and when highlighted press **ENTER** key, or use shortcut - press key **E**). This action begins by performing the automatic nulling which in this case is only in effect for the duration of the calibration process. It will not affect EM61-MK2 readings. After the nulling is completed (less than 5 seconds) the External QC coil Calibration window is displayed.



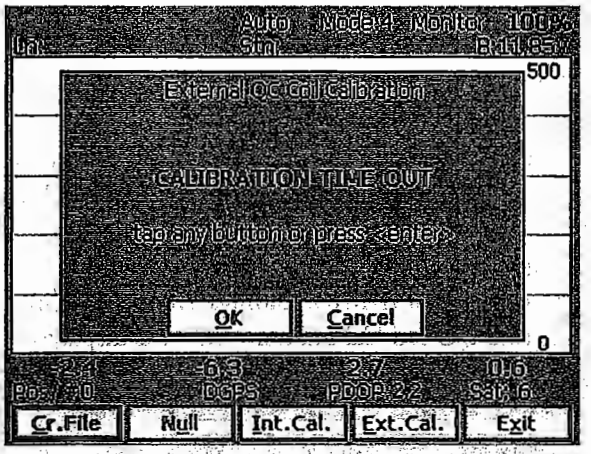
After **OK** button is tapped (or shortcut key **O** is pressed) the window displays timer with elapsed seconds and EM61-MK2 readings. This display lasts for 60 seconds. During this time please follow the instructions provided on the Allegro screen.



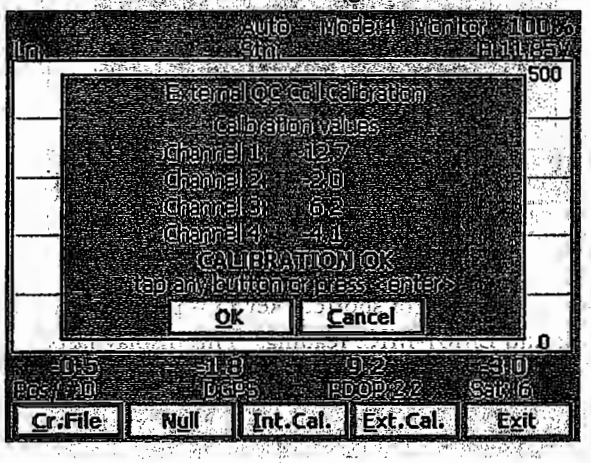
External QC coil calibration can end in the following four ways:

The process can be stopped by an operator at any time by tapping **Cancel** button or pressing shortcut key **C**.

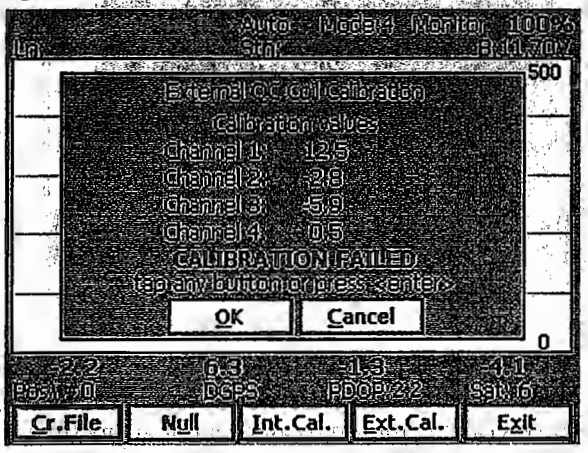
The calibration may end by time out (60 seconds) if the External QC coil button was not pressed or this action did not activate QC coil. The following window will then be displayed (see below).
After pressing any key the program returns to Monitoring window. To repeat External QC coil calibration please tap the **Int.Cal.** button again.



The logger will determine if the instrument has passed test. If after activating the QC coil, the program determines that the reading is inside the standard values within +/- 10% tolerances then a message "CALIBRATION OK" will be displayed.



Otherwise, if the program determines that the reading is outside of the test values range the corresponding message "CALIBRATION FAILED" is displayed.



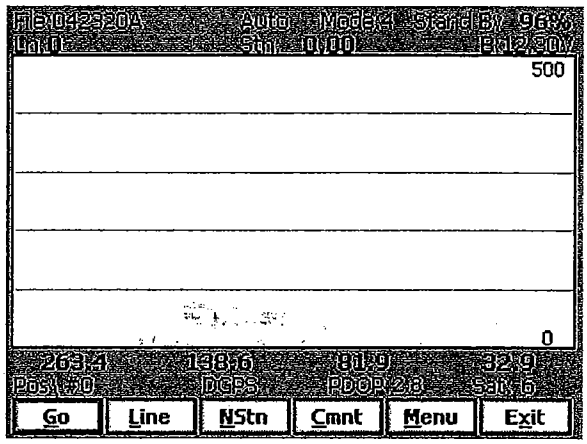
Regardless of the test result (OK or FAILED) the readings will be saved on screen. The program returns to Monitoring window after any button is tapped or ENTER key is pressed. Then the Internal QC coil calibration process can be repeated.

Exit (exit Monitor mode)

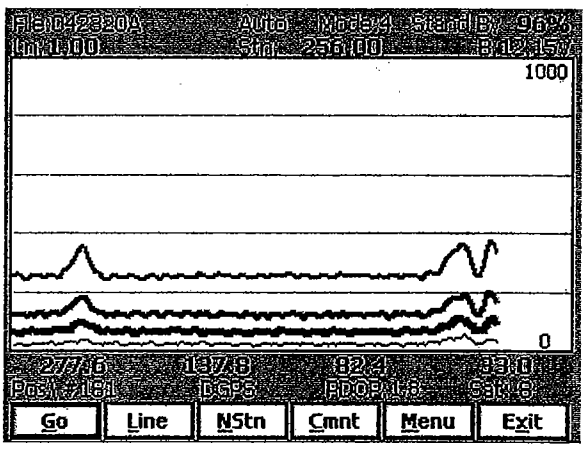
After tapping Exit button (or executing this option using keyboard) the program immediately returns to Main Screen.

6.2 Stand By Mode

After data file is created in Monitoring mode the program automatically switches logging window to Stand By mode. This windows is similar to Monitor mode however it contains survey parameters (file name, survey line name, etc.) and different set of options represented by buttons displayed at the bottom of the screen. The logging window in Stand By mode in initial state (before any data is recorded) is presented below.



The main portion of the screen is occupied by the plot area which displays profiles (see Figure below which shows Stand By mode after some data were collected). Readings in the plot area can be displayed in compressed amplitude scale, which corresponds to Square Root of the amplitude. In compressed amplitude scale 0 to 100 corresponds to 0 to 10,000 mV, and compressed range 0 to 200 corresponds to 0 to 40,000 mV. Plotting data in compressed amplitude allows you to show details in the low range of amplitude, as well as relatively good resolution in the high range of data on the small screen. **Please note, that data displayed in the numeric form are always given in the standard, linear scale.** The amplitude scale is divided by four or five grey grid lines. In the case where the amplitude scale starts with a negative value, then the grid line corresponding to zero is always plotted as a thicker line.



Readings for channels 1, 2, 3, and 4 (or T) are shown in numeric form below the plot area. Channel labels are not displayed due to the small screen of the Allegro. Values of readings are displayed in the following order (from the left): Channel 1, 2, 3, and 4 (or T). EM61-MK2 readings (in numeric form) are updated in Stand By mode approximately 10 times per second. Profiles in the plot area are updated only during Logging mode when data are actually saved in the data file.

A section of the window at the top of the screen contains two lines of text displaying survey and instrument related parameters. These are (from top left): current data file name (labeled **File:**), survey mode (**Auto, Wheel** or **Manual**), instrument mode **4** or **D** (labeled Mode:)), logging mode **Stand By** or **Logging**), Allegro internal battery level (in % of full charge, not labeled), current survey line (labeled **Ln:**), current station (labeled **Stn:**), and EM61-MK2 battery level in Volts (labeled **B:**). When fiducial marker is active a label **M** is displayed between station label and station value.

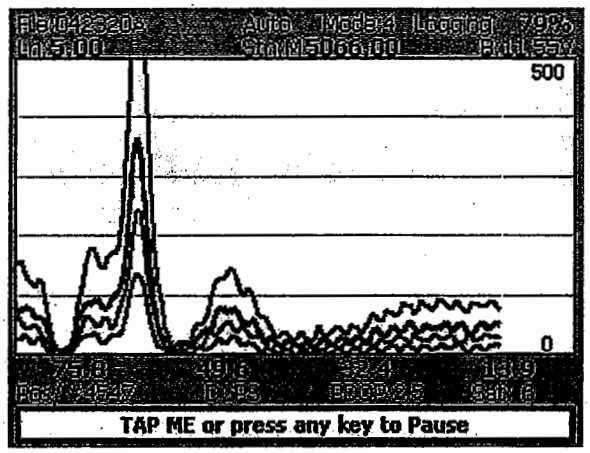
In the Stand By mode the station number will not change. Stations in the EM61MK2 program are incremented by station increment value after each reading is written to the data file.

One line of the display is dedicated to showing the GPS status. A number following the label **Pos/#** provides the number of GPS positions saved in the current data file. In Stand By mode the number of positions is not incremented (it is updated only when GPS position is written to the file). However this label indicates GPS activity by toggling between forward (/) and back (\) slash (that follows label **Pos**) every time the program receives a message from GPS receiver. If the slash is not changing for long periods of time (larger than GPS receiver update rate) it means that the GPS receiver is not working or that it is not connected to the field computer. A label **DGPS** (Differential Global Positioning System) indicates that GPS readings are differentially corrected in real time, while label **AGPS** (Autonomous Global Positioning System) indicates lack of differential correction. The next label **PDOP** with a value varying between 0 and 99.9 represents an index called Position Dilution of Precision (**PDOP**). This value is available only when messages both, GGA and GSA are received from GPS. The last label Sat and following number shows number of currently tracked satellites. Refer to section 4 (Set Port for GPS), Appendix A, and to GPS manuals for more information about GPS parameters.

Several available field options are listed at the bottom (in form of buttons) of the Stand By mode window. They will be described in the following section 6.4.

6.3 Logging Mode

The Logging mode is enabled by tapping on the **GO** button or pressing the shortcut key **G** (or the **<ENTER>** key if button **GO** is highlighted) in Stand By mode. After this button is pressed the list of buttons at bottom of the screen will be replaced by one "Pause" button, label Stand By will be replaced by label **Logging** (at the top of the display) and data will be logged in the mode corresponding to the selected EM61-MK2 mode in the Survey Setup menu. All labels and parameters (with the exception of buttons representing Stan By mode options) are the same as in Stand By mode and they are described in the preceding section 6.2. The screen in Logging mode is presented below.



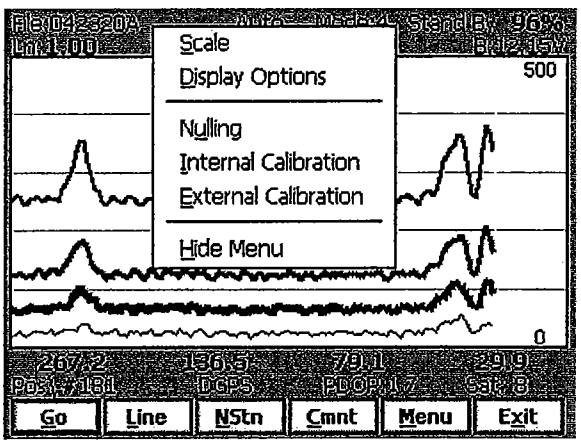
After the screen changes to Logging mode the current station (label **Stn:**) is updated according to the station interval. Similarly, if GPS Input was enabled, total number of GPS positions (label **Pos**) in the data file is incremented every time (usually once a second) GPS position is written to the file. Profile curves (for channels selected in Display Options window) are updated after each reading is written to the data file.

There is only one option available in the Logging mode - pause logging. After a Pause button is tapped or Pause key (any key or other Pause Key selected in Logger Setup window) is pressed the recording is stopped and the Logging mode returns to the Stand By mode. In Stand By mode the EM61-MK2 data will be displayed with the update rate approximately 10 readings per second, however data will not be saved in the log file and profile curves will be not updated.

Exit from the logging session and access to field options are available only from the logging window in Stand By mode.

6.4 Stand By Mode Field Options

Several field options are available while the Logging window is in the Stand By mode. More frequently used options can be accessed directly from command buttons and others can be used from pop up menu activated by button **Menu** (displayed below). Command buttons can be used by tapping on the desired button, or from the keyboard by pressing one of the shortcut keys (underlined characters on button labels) or by navigating using <**TAB**> key (sets button as a default button - default button is highlighted) and pressing <**ENTER**> key.



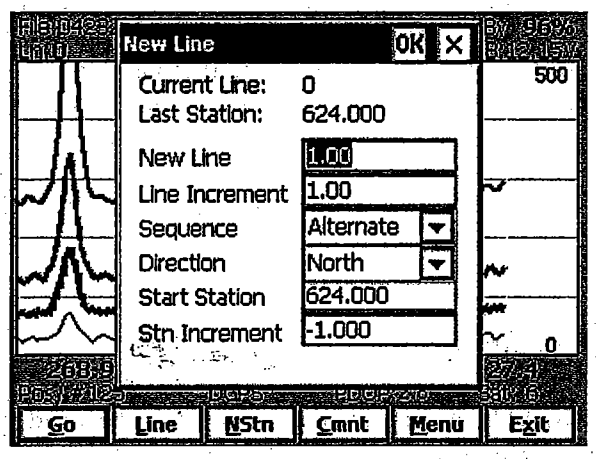
Options listed in the menu can be accessed directly (without displaying pop up menu from Menu button) by using keyboard shortcuts, i.e. pressing key S will display Scale dialog. While menu is displayed options can be selected by tapping on the appropriate proper option, or from the keyboard by pressing the shortcut keys or by navigating using <**Up**> and <**Down**> arrow keys and executing by <**ENTER**>

GO *(start data logging)*

Tap on the **GO** button, or while using the keyboard press shortcut key <**G**> or if the button is a default button (highlighted) press <**ENTER**>. The logging window in Stand By mode will change to Logging mode and logging data starts immediately.

Line *(New Survey Line)*

The New Line dialog is displayed (see Figure below). Selecting this option allows the operator to enter a new survey line number (name) and associated line parameters (Line Increment, Line Sequence, Direction, Start Station, and Station Increment). The new line number and associated parameters are prompted by the program based on parameters specified in the Survey Setup menu.



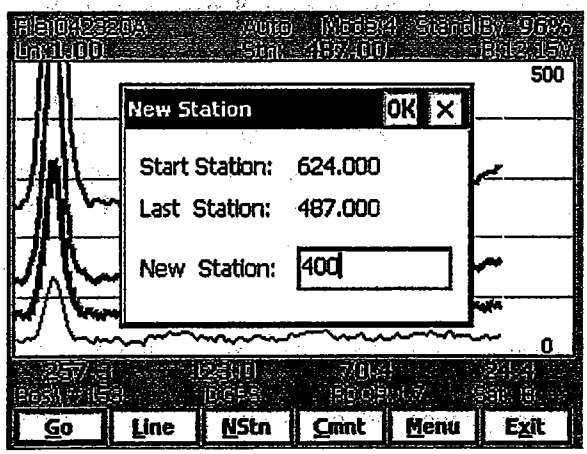
At the top of the dialog the last survey line name and the last logged station are displayed. Default name for the new line is given based on the Line Increment parameter. The default Start Station, direction of the Station Increment, and Direction are determined based on Sequence selection. All these parameters can be overwritten by the user as described in the Survey Setup menu description (chapter 2).

After all the parameters in the New Line dialog are updated tap the button **OK** or press **ENTER** key to accept the displayed settings. The program will return to the Logging window in Stand By mode. Survey line (**Ln:**) name and current station (**Stn:**) value will be updated and profile curves plot for former survey line will disappear.

To return to Stand By mode and current survey line settings (state before this dialog was selected) tap **Cancel** (X) button or press **Esc** key, the dialog window will disappear.

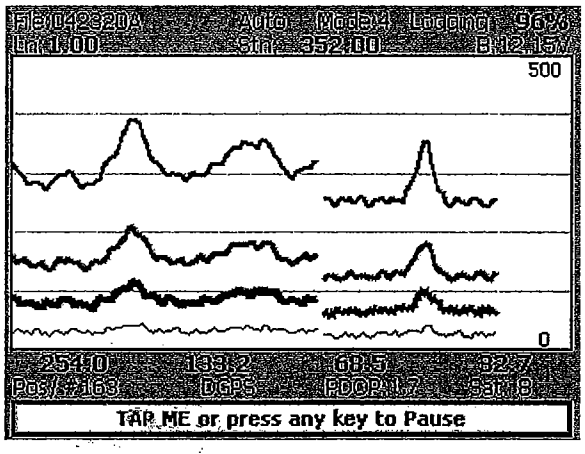
NStn *(New Station)*

Selecting this option allows the operator to enter a new station number (within the same survey line). The New Station dialog is displayed.



Start and Current station are displayed at the top of the dialog. The New Station can be entered in the provided edit box labeled New Station.

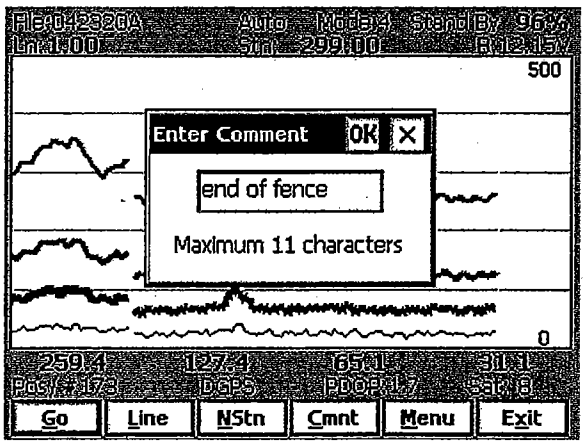
Tap the button **OK** or press **ENTER** key to accept the new value. The program will return to the Logging window in Stand By mode. Current station (**Stn:**) value will be updated and after data logging is activated the profile curves will have a small gap (two pixels) showing the new station entry (see Figure below).



To return to Stand By mode and current survey line settings (state before this dialog was selected) tap **Cancel** (X) button or press **Esc** key, the dialog window will disappear and measurements can be continued.

Cmnt *(Comment)*

Selecting this option allows the operator to enter a comment at any point of the survey. A maximum of 11 characters can be entered as a comment. The Enter Comment dialog is displayed.

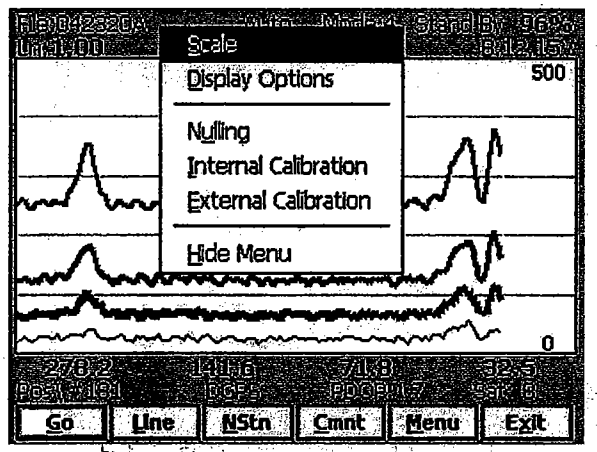


Tap the button **OK** or press **ENTER** key to accept the comment entered in a text box of the dialog. The text of the comment is saved in the file with a corresponding time stamp and the program will return to the Logging window in Stand By mode.

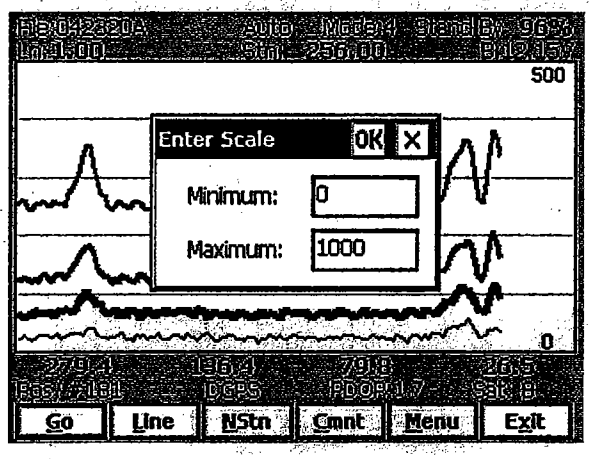
To ignore an entry and return to Stand By mode tap **Cancel** (X) button or press **Esc** key, the dialog window will disappear and measurements can be continued.

Scale *(New Scale for Profile Plot)*

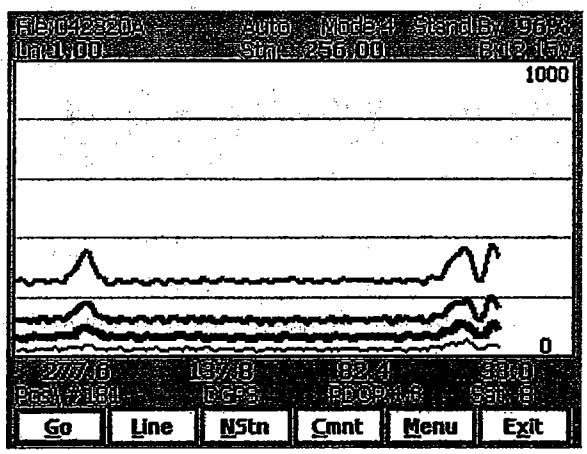
Selecting New Scale option allows the operator to enter new scale parameters for the profile plot. This option is available only from pop up menu (accessible from **Menu** button) or directly from keyboard by using shortcut key <S>.



The Enter Scale dialog will be displayed. It contains two text boxes for Minimum and Maximum values of a new scale for profile plot. Current settings (minimum and maximum values) for the scale are displayed in the bottom right and top right corners of the plot area.



After minimum and maximum values are specified tap the button **OK** or press **ENTER** key to accept to accept new values and the profile plot area will be redrawn (see Figure below).

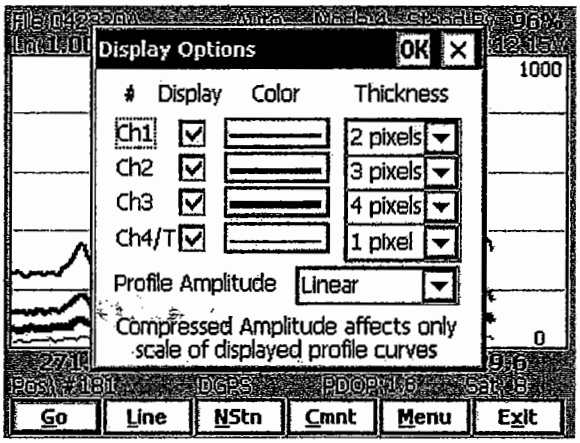


To ignore an entry and return to Stand By mode tap the **Cancel** (X) button or press **Esc** key, the dialog window will disappear and measurements can be continued.

Display Options *(new options for profile plot display)*

This option is available only from pop up menu (accessible from **Menu** button) or directly from keyboard by using shortcut key <**D**>.

After the **Display Options** item was selected in the pop up menu the Display Options dialog window appears on the screen. This dialog allows you to enable and disable the display of each channel profile, specify color and thickness of profiles, and select linear or compressed amplitude for profiles. The dialog is presented below.



Please refer to chapter 5 where this dialog and its parameters are described in detail.

Tap the button **OK** or press **ENTER** key to accept updated display parameters. The dialog will disappear and profile plot area will be redrawn in Stand By mode.

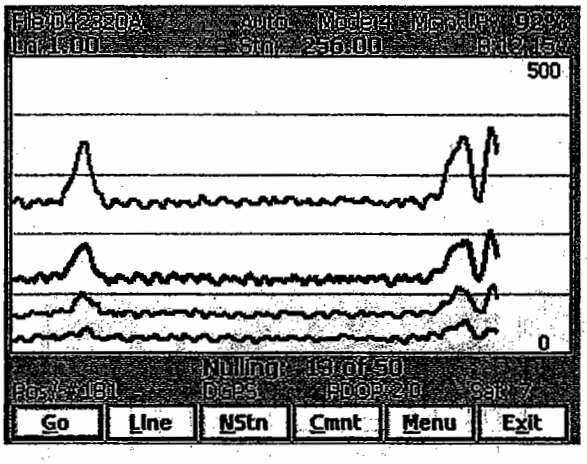
To return to Stand By mode and current display options (state before this dialog was selected) tap **Cancel** (X) button or press **Esc** key, the dialog window will disappear.

Nulling

This option is available only from pop up menu (accessible from **Menu** button) or directly from keyboard by using shortcut key <**U**>.

During data collection (in Stand By mode) a confirmation message will be displayed (there is no such message if Nulling is performed in Monitoring mode) before actual operation is applied.

After above message is confirmed the program collects 50 readings and calculates the instrument offset.

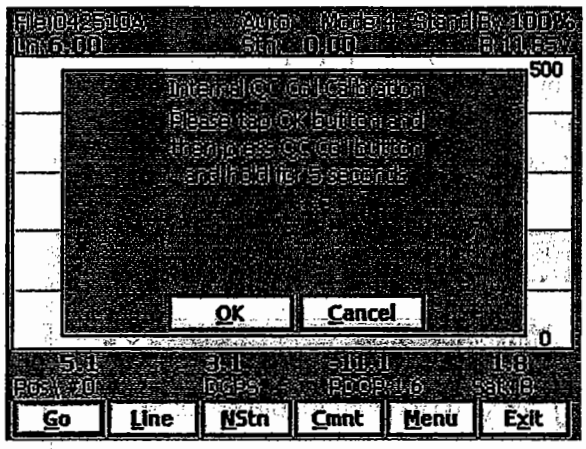


The calculated offset is applied to all the readings that follow this operation. If needed, this procedure can be repeated several times until satisfactory results are obtained. However, there is no associated "Undo" function. If original values (without calculated offsets) of the EM61-MK2 readings are needed, exit the EM61MK2 program and run it again. The EM61-MK2 instrument does not have to be turned OFF.

Internal Calibration *(Internal QC coil calibration)*

The Internal QC coil calibration is described in detail in the EM61-MK2 Operating Instructions. During data logging in Stand By mode this option is available only from the pop up menu (accessible from **Menu** button) or directly from the keyboard by using shortcut key **<I>**.

The Internal Calibration process begins by performing the automatic nulling which in this case is only in effect for the duration of the calibration process. It will not affect EM61-MK2 readings. After the nulling is completed (less than 5 seconds) the Internal QC Coil Calibration window is displayed.

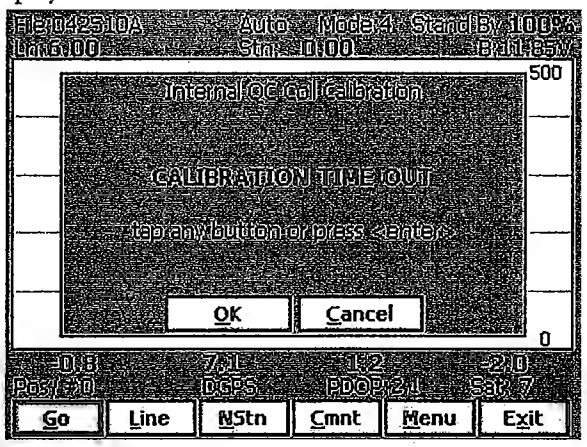


After **OK** button is tapped (or shortcut key **O** is pressed) the window displays timer with elapsed seconds and EM61-MK2 readings. This display lasts for 60 seconds. During this time please follow the instructions provided on the Allegro screen.

Internal QC coil calibration can end in the following four ways:

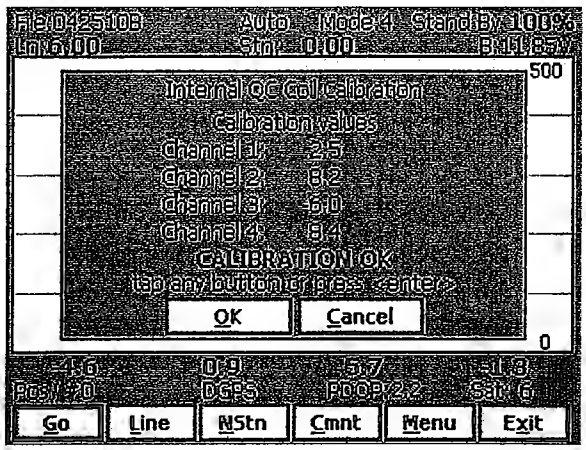
The process can be stopped by an operator at any time by tapping **Cancel** button or pressing shortcut key C.

The calibration may end by time out (60 seconds) if QC coil button was not pressed or this action did not activate QC coil. The following screen will then be displayed:

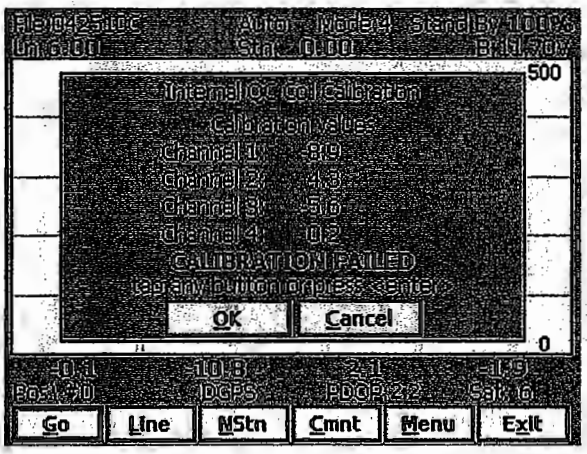


After pressing any key the program returns to logging window in Stand By mode. To repeat Internal QC coil calibration please repeat the procedure.

The logger will determine if the instrument has passed test. If after activating the QC coil, the program determines that the reading is inside the standard values within +/- 10% tolerances then a message "CALIBRATION OK" will be displayed (see below).



Otherwise, if the program determines that the reading is outside of the test values range the corresponding message "CALIBRATION FAILED" is displayed.

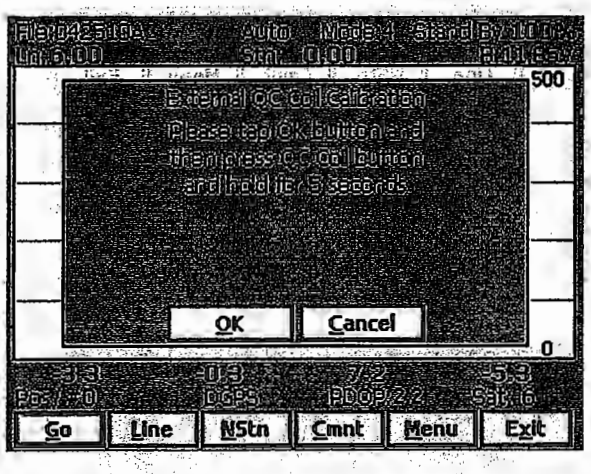


Regardless of the test result (OK or FAILED) the readings will be saved on screen. The program returns to logging window in Stand By mode after any button is tapped or ENTER key is pressed. Then the Internal QC coil calibration process can be repeated.

External Calibration *(External QC coil calibration)*

The External QC coil calibration option is described in detail in the EM61-MK2 Operating Instructions. During data logging (when logging window is in Stand By mode) this option is available only from pop up menu (accessible from **Menu** button) or directly from keyboard by using shortcut key <**E**>.

The External calibration action begins by performing the automatic nulling which in this case is only in effect for the duration of the calibration process. It will not affect EM61-MK2 readings. After the nulling is completed (less than 5 seconds) the External QC coil Calibration window is displayed.

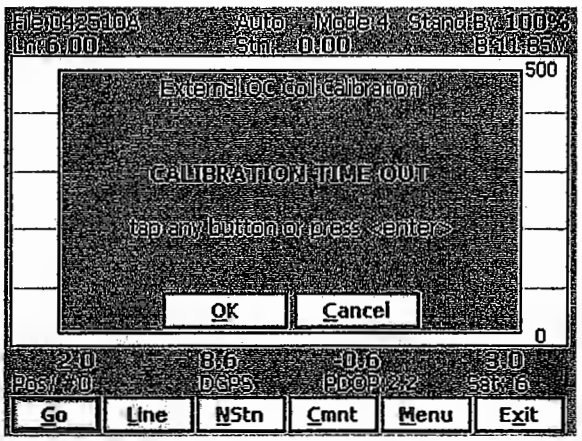


After the **OK** button is tapped (or shortcut key **O** is pressed) the window displays a timer with elapsed seconds and EM61-MK2 readings. This display lasts for 60 seconds. During this time please follow the instructions provided on the Allegro screen.

External QC coil calibration can end in the following four ways:

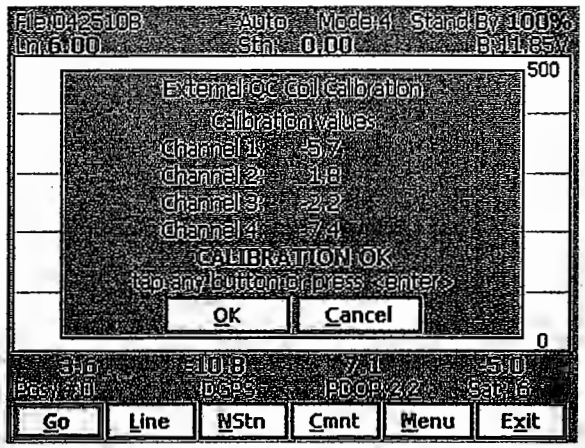
The process can be stopped by an operator at any time by tapping **Cancel** button or pressing shortcut key **C**.

The calibration may end by time out (60 seconds) if the External QC coil button was not pressed or this action did not activate QC coil. The following window will then be displayed (see below).

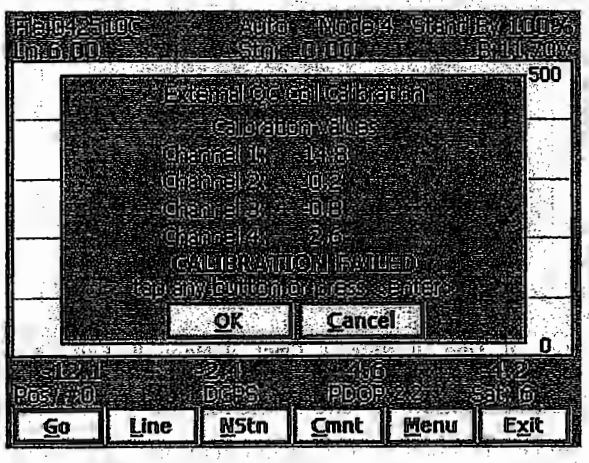


After pressing any key the program returns to Stand By mode window. To repeat External QC coil calibration please repeat the procedure.

The logger will determine if the instrument has passed test. If after activating the QC coil, the program determines that the reading is inside the standard values within +/- 10% tolerances then a message "CALIBRATION OK" will be displayed.



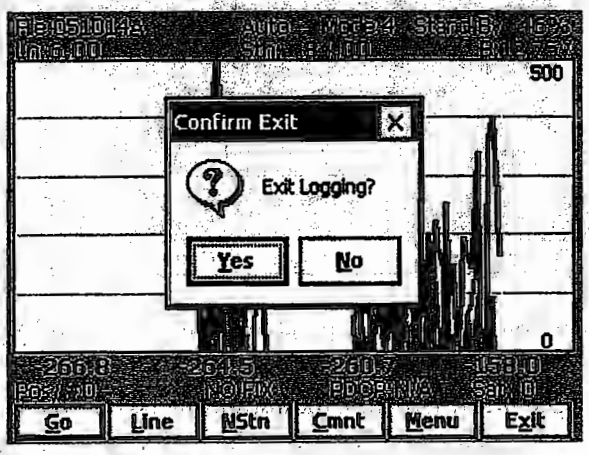
Otherwise, if the program determines that the reading is outside of the test values range the corresponding message "CALIBRATION FAILED" is displayed.



Regardless of the test result (OK or FAILED) the readings will be saved on screen. The program returns to Monitoring window after any button is tapped or ENTER key is pressed. Then the Internal QC coil calibration process can be repeated.

Exit *(exit data logging)*

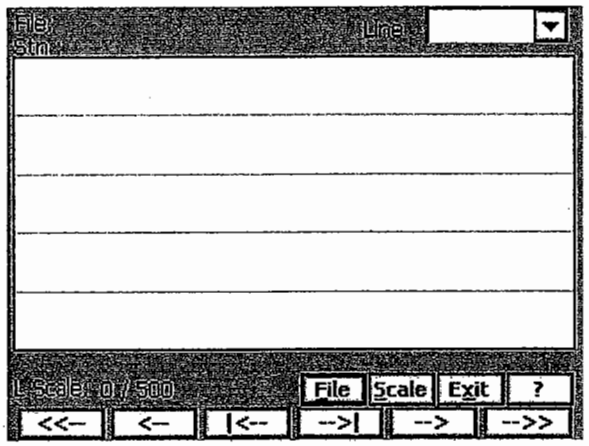
During data collection (in Stand By mode) a confirmation message will be displayed (there is no such message if **Exit** is performed in Monitoring mode) before program exits logging window.



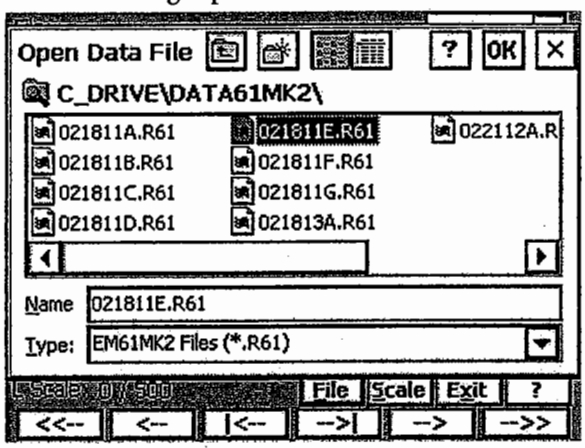
After above message is confirmed the program stops logging, closes data file and returns to Main Screen.

7. View Data Files

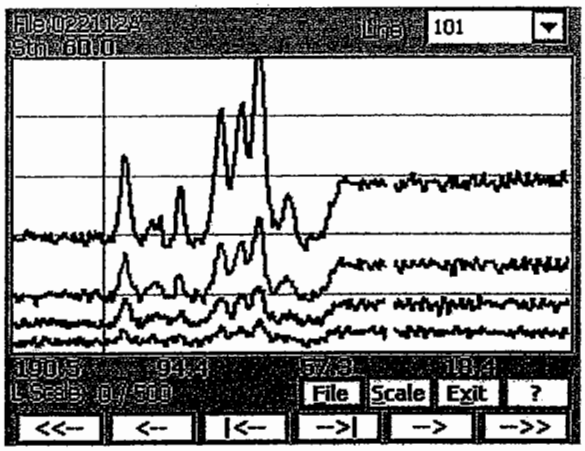
This option allows you to view recorded data files. After the View Files button is tapped (or executed from the keyboard) in the Main Screen the View Data Files window will be displayed.



To open the data file tap the button labeled **File** or execute this option using the keyboard (navigate to the button by pressing **TAB** key and when highlighted press **ENTER** key, or use shortcut - press key **F**). The Open Data File dialog is presented below.



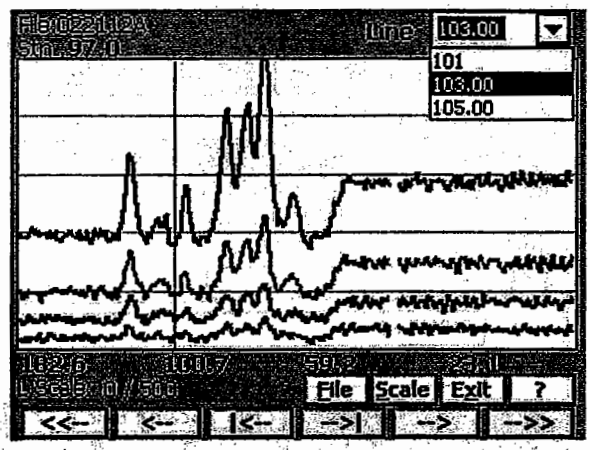
The file name can be selected in the Open Data File dialog using the Windows standard interface procedure. After the file is selected (highlighted) tap the button **OK** or press **ENTER** key to accept and display data file (to cancel selection tap **Cancel** (X) button or press **Esc** key). After the file is opened readings taken at the beginning of the first survey line in the file are displayed, as shown below.



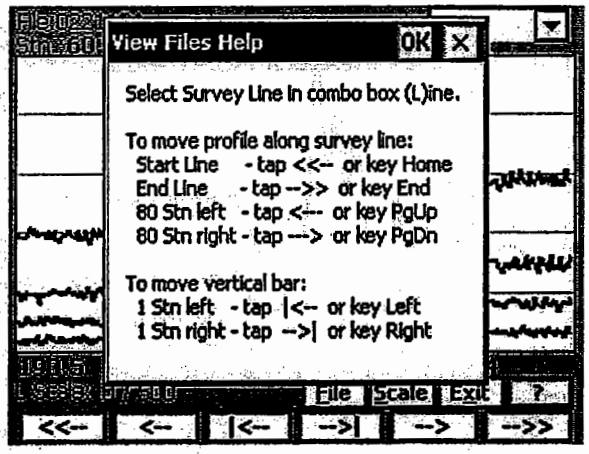
Name of the currently displayed data file is shown in the left top corner of the window. The main portion of the screen is occupied by the plot area which displays profiles. Readings in the plot area can be displayed in linear or compressed amplitude scale. Amplitude scale as well as display range (minimum and maximum value) is given by label located at the left bottom of the window (i.e. **L Scale: 0/500** means linear scale from 0 to 500 mV). The amplitude scale is set only in the Display Options window (see chapter 5) and range of scale display can be changed by tapping the button labeled **Scale**. The plot area is divided by four or five grey grid lines. In cases where the amplitude scale starts with a negative value, then the grid line corresponding to zero is always plotted as a thicker line.

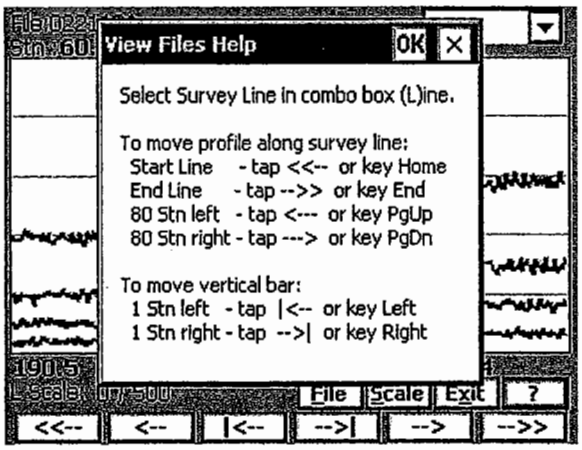
A vertical bar (grey vertical line) indicates currently displayed station. The station is displayed above the plot area, next to label **Stn:** and readings at this station for channels **1, 2, 3,** and **4** (or **T**) are shown in numeric form below the plot area. Channel labels are not displayed due to the small screen of the Allegro. Values of readings are displayed in the following order (from the left): Channel 1, 2, 3, and 4 (or T). EM61-MK2 readings (in numeric form) are updated every time vertical bar is moved.

To change the currently displayed survey line use the drop-down box labeled **Line** located in the top right corner of the window. Tapping on the down arrow next to the text box labeled **Line** opens a drop-down box showing the available survey lines. When the keyboard is being used you can activate the text box by pressing the **TAB** key until the drop down box is highlighted and then by using Up or Down arrow keys select one of available lines (as shown below).



To shift the range of the displayed stations and to move the vertical bar indicating the currently displayed station, use the buttons located along the bottom of the View Files window. These buttons can be activated by tapping or by pressing the keyboard keys. A help screen containing info related to each button can be displayed at any time by tapping (or executing from keyboard) the Help button labeled **?**. The Help screen is shown below.





When moving displayed profile along survey line:

button labeled <<-- or key **Home** moves display to the start of the currently displayed survey line, the left most station is the start station of the line,

button labeled -->> or key **End** moves display to the end of the currently displayed survey line, the right most station is a final station of the survey line,

button labeled <--- or key **PgUp** moves display 80 stations to the left,

button labeled ---> or key **PgDn** moves display 80 stations to the right.

When changing stations and corresponding readings:

button labeled |<-- or key **Left** (left arrow) moves vertical bar (station) one station to the left,

button labeled -->| or key **Right** (right arrow) moves vertical bar (station) one station to the right.

To exit the View Files window tap the button labeled **Exit** (or from keyboard use shortcut key **X** or press key **ENTER** when the button is highlighted) to close file (if open). The program will return to Main Screen.

Appendix A

A.1 Description of Data File in EM61MK2 Allegro CX Format

Each record contains 24 characters, including line feed at the end of each record.

Header of the file (contains six records starting with characters E, H, O, O, O, and O)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
E	M	6	1	M	K	2		W	1	0	0	Survey Type			UT	IT	IM						10
H		File Name										Time Increment [s] (F7.3)												10
O	Offset for Ch1 (F9.2)										IC	QC coil value for Ch1 (F9.2)											10
O	Offset for Ch2 (F9.2)										IC	QC coil value for Ch2 (F9.2)											10
O	Offset for Ch3 (F9.2)										IC	QC coil value for Ch3 (F9.2)											10
O	Offset for Ch4 (F9.2)										IC	QC coil value for Ch4/T (F9.2)											10

EM61MK2	-	identification of program file
W100	-	version number (1.00, W - indicates file created by Windows CE program)
Survey Type	-	GPS (if GPS Input Enabled) or GRD (grid)
UT	-	unit type (0 = meters, 1 = feet)
IT	-	instrument type (0 =sensor 1x0.5m, 1 = 1x1m, 2 = 0.5x0.5m, 3 = HH61)
IM	-	instrument mode (0 =Auto, 1 =Wheel, and 2 =Manual)
File Name	-	file name, maximum 8 characters
Time Increment	-	time increment (Auto Mode) in seconds
Offset	-	offset for indicated channels in mV
IC	-	QC coil calibration (=N not performed, <>N otherwise)
QC coil value	-	value of QC coil calibration for indicated channels in mV
10	-	Line Feed character

Header at the start of survey line (eight records starting with L, B, A, Z, O, O, O, O)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
L	Line Name (8 characters)																						10
B	Start Station (Format F11.2)																						10
A	Dir							Station Increment (Format F11.2)															10
Z	D	D	M	M	Y	Y	Y	Y		H	H	:	M	M	:	S	S						10
O	Offset for Ch1 (F9.2)											Former Offset for Ch1 (F9.2)											10
O	Offset for Ch2 (F9.2)											Former Offset for Ch2 (F9.2)											10
O	Offset for Ch3 (F9.2)											Former Offset for Ch3 (F9.2)											10
O	Offset for Ch4 (F9.2)											Former Offset for Ch4/T (F9.2)											10

Line Name	-	Line Name, maximum 8 characters
Start Station	-	Start Station for the Line, format F11.2
Dir	-	Direction of the Line (E, W, N, or S)
Station Inc.	-	Station Increment, format F11.3
Date	-	Date when Line was created, format DD-MM-YYYY
Time	-	Real Time when Line was created, format HH:MM:SS
Offset	-	Offset for indicated channels in mV at the start of Line
Former Offset	-	Former offset for indicated channels in mV
10	-	Line Feed character

Timer Relation

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
*	Computer Time (Format HH:MM:SS.sss)												Time Stamp in milliseconds										10

Indicates relation between computer clock and the program timer. This record links timer in milliseconds and computer time (local time) in format HH:MM:SS.sss. This record is written to the file each time a new new line is entered.

Reading

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
I	Gn	1h	1l	2h	2l	3h	3l	4h	4l	5h	5l	6	Time Stamp in ms (10 digits)										10

I	-	indicator T, D, E, F, M, N, P, or Q. Each record representing reading starts with one of the following character, which indicates type of reading:	
		T - Standard, Mode 4,	channels 1, 2, 3, 4
		D - Standard, Mode D,	channels 1, 2, 3, T
		E - Hand Held, Mode 4,	channels 1, 2, 3, 4
		F - Hand Held, Mode D,	channels 1, 2, 3, T
		M - Standard, Mode 4,	channels 1, 2, 3, 4 +Marker
		N - Standard, Mode D,	channels 1, 2, 3, T +Marker
		P - Hand Held, Mode 4,	channels 1, 2, 3, 4 +Marker
		Q - Hand Held, Mode D,	channels 1, 2, 3, T +Marker
Gn	-	one character parameter (Hex format), contains Gain, see table of ranges at the end of this section.	
1h	-	higher byte of the 2's complement Hex number of Channel 1	
1l	-	lower byte of Channel 1	
2h	-	higher byte of the 2's complement Hex number of Channel 2	
2l	-	lower byte of Channel 2	
3h	-	higher byte of the 2's complement Hex number of Channel 3	
3l	-	lower byte of Channel 3	
4h	-	higher byte of the 2's complement Hex number of Channel 4	
4l	-	lower byte of Channel 4	
5h	-	higher byte of the 2's complement Hex number of TX current	
5l	-	lower byte of TX current	
6	-	fraction of current (5h 5l), Hex number	
Time Stamp	-	time in ms from the Windows start (resets every 49.7 days)	
10	-	Line Feed character	

Comment

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
C	Comment (maximum 11 characters)												Time Stamp in ms (10 digits)										10

New Station

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
S	New Station (Format 11.2)												Time Stamp in ms (10 digits)										10

Nulling

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
O	Offset for Ch1 (F9.2)											Former Offset for Ch1 (F9.2)											10
O	Offset for Ch2 (F9.2)											Former Offset for Ch2 (F9.2)											10
O	Offset for Ch3 (F9.2)											Former Offset for Ch3 (F9.2)											10
O	Offset for Ch4 (F9.2)											Former Offset for Ch4/T (F9.2)											10

QC Coil Calibration

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
I	C	Offset for Ch1 (F9.2)																					10
I	C	Offset for Ch2 (F9.2)																					10
I	C	Offset for Ch3 (F9.2)																					10
I	C	Offset for Ch4 (F9.2)																					10

IC - **II** indicates Inrenal QC coil calibration,
IE indicates External QC coil calibration.

GPS Data Message Records

Each GPS record (GGA Message) is broken in to several 22 characters strings and placed in the EM61MK2 data file which contains 24 characters records, including one character indicator and line feed at the end of each record. The GPS sequence starts at the line which contains character @ as the first character, then records that contain continuation of the same message start with character #. The GPS sequence ends with a line starting with the character !. The last line contains logger time stamp in milliseconds for given GPS reading. A sample of the GPS message written in EM61MK2 format is given below.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
@	$	G	P	G	G	A	,	h	h	m	m	s	s	.	s	s	,	d	d	m	m	.	10
#	m	m	m	m	m	,	s	,	d	d	d	m	m	.	m	m	m	m	m	,	s	,	10
#	n	,	q	q	,	p	p	.	p	,	s	a	a	a	a	a	.	a	a	,	u	,	10
#	±	x	x	x	x	.	x	,	M	,	s	s	s	,	a	a	a	*	c	c	CR	LF	10
!													Time Stamp in milliseconds										10

The GPS sequence may contain 4 to 6 records. Component of the GGA message may differ in length, however they are placed in the same number of columns. Refer to Appendix B (section B.2) for definition of each component of GGA data message.

A.2 Conversion Factors

EM61MK2 has four channels. Channels 1, 2, and 3 are common for Mode 4 and Mode D. Channel 4 in Mode D is named Channel T (it corresponds to Top coil).

The instrument response is converted to output voltage in mV for each sampling channel as given below.

Channel 1 to 4 - converted data
DATA1 (to 4) - instrument output for each channel as recorded in logger
RANGE - range is controlled by the EM61MK2, it can be 1, 10, 100

Standard Unit - Mode 4 (One Sensor 1 x 0.5 m or 1 x 1 m)

Channel 1=(DATA1 x 4.8333 x 2)/RANGE
Channel 2=(DATA2 x 4.8333 x 2)/RANGE
Channel 3=(DATA3 x 4.8333 x 2)/RANGE
Channel 4=(DATA4 x 4.8333 x 2)/RANGE

Standard Unit - Mode D (Two Sensors 1 x 0.5 m or 1 x 1 m, Top and Bottom coils))

Channel 1=(DATA1 x 4.8333 x 2)/RANGE
Channel 2=(DATA2 x 4.8333 x 2)/RANGE
Channel 3=(DATA3 x 4.8333 x 2)/RANGE
Channel T=(DATA4 x 4.8333 x 4)/RANGE

if coil is 1 x 0.5 m Channel T is further multiplied by a factor 1.114.

Hand Held Unit - Mode 4 (One Sensor)

Channel 1 = 0.902500 x (DATA1 x 4.8333)/RANGE
Channel 2 = 1.363000 x (DATA2 x 4.8333)/RANGE
Channel 3 = 2.026795 x (DATA3 x 4.8333)/RANGE
Channel 4 = 3.018856 x (DATA4 x 4.8333)/RANGE

Hand Held Unit - Mode D (Two Sensors, Top and Bottom coils))

Channel 1 = 0.9025 x (DATA1 x 4.8333)/RANGE
Channel 2 = 1.3630 x (DATA2 x 4.8333)/RANGE
Channel 3 = 2.0430 x (DATA3 x 4.8333)/RANGE
Channel T = 12.152 x (DATA4 x 4.8333)/RANGE

Further each channel is normalized by current following formula:

Standard Unit

Channel = Channel x 3000/Current

Hand Held Unit

Channel = Channel x 1800/Current

where, current is a value represented by **5h**, **5l**, and **6** in EM61MK2 data file (see section B.1)

Table of Ranges Determined by the EM61-MK2 Microprocessor

HEX	Ch1	Ch2	Ch3	Ch4
0	1	1	1	1
1	1	1	1	10
3	1	1	1	100
4	1	1	10	1
5	1	1	10	10
7	1	1	10	100
C	1	1	100	1
D	1	1	100	10
F	1	1	100	100
10	1	10	1	1
11	1	10	1	10
13	1	10	1	100
14	1	10	10	1
15	1	10	10	10
17	1	10	10	100
1C	1	10	100	1
1D	1	10	100	10
1F	1	10	100	100
30	1	100	1	1
31	1	100	1	10
33	1	100	1	100
34	1	100	10	1
35	1	100	10	10
37	1	100	10	100
3C	1	100	100	1
3D	1	100	100	10

HEX	Ch1	Ch2	Ch3	Ch4
40	10	1	1	1
41	10	1	1	10
43	10	1	1	100
44	10	1	10	1
45	10	1	10	10
47	10	1	10	100
4C	10	1	100	1
4D	10	1	100	10
4F	10	1	100	100
50	10	10	1	1
51	10	10	1	10
53	10	10	1	100
54	10	10	10	1
55	10	10	10	10
57	10	10	10	100
5C	10	10	100	1
5D	10	10	100	10
5F	10	10	100	100
70	10	100	1	1
71	10	100	1	10
73	10	100	1	100
74	10	100	10	1
75	10	100	10	10
77	10	100	10	100
7C	10	100	100	1
7D	10	100	100	10

HEX	Ch1	Ch2	Ch3	Ch4
C0	100	1	1	1
C1	100	1	1	10
C3	100	1	1	100
C4	100	1	10	1
C5	100	1	10	10
C7	100	1	10	100
CC	100	1	100	1
CD	100	1	100	10
CF	100	1	100	100
D0	100	10	1	1
D1	100	10	1	10
D3	100	10	1	100
D4	100	10	10	1
D5	100	10	10	10
D7	100	10	10	100
DC	100	10	100	1
DD	100	10	100	10
DF	100	10	100	100
F0	100	100	1	1
F1	100	100	1	10
F3	100	100	1	100
F4	100	100	10	1
F5	100	100	10	10
F7	100	100	10	100
FC	100	100	100	1
FD	100	100	100	10

A.3 Example of Data File in EM61MK2 (Allegro CX) Format

The Em61MK2 data file records are written in binary format, therefore the file may have different shape when displayed or printed, depending on particular video or pronter settings.

```
EM61MK2 W100GPS000
H 042320A    0.200
0      0.00E      0.00
0      0.00E      0.00
0      0.00E      0.00
0      0.00E      0.00
L0
B        0.00
AS             1.000
Z23042005 20:02:51
0      0.00       0.00
0      0.00       0.00
0      0.00       0.00
0      0.00       0.00
*20:02:51.000   4179829
@$GPGGA,020412.00,4336.
#59410,N,07936.64856,W,
#2,6,2,141.56,M,-35,M,5
#,119*55
!                4287423
@$GPGSA,A,3,30,,,25,,20
#,,14,,06,,01,02.8,02.1
#,02.0*0D
!                4287441
Eÿø     `/^ "N   4287673
Eÿ      t/" "Q   4287879
C comment text   4287983
Eÿ:     G/yï "O  4288089
Eÿš     h/¼þ "W  4288279
@$GPGGA,020413.00,4336.
#59408,N,07936.64857,W,
#2,6,2,141.51,M,-35,M,6
#,119*58
!                4288338
Eÿ¶     5/ # "S  4288488
@$GPGSA,A,3,30,,,25,,20
#,,14,,06,,01,02.8,02.1
#,02.0*0D
!                4288419
Eÿþ     º/j "O   4288677
EÿL     t/k "Q   4288885
@$GPGGA,020414.00,4336.
#59411,N,07936.64846,W,
#2,6,2,141.68,M,-35,M,6
#,119*5D
!                4289337
Eÿ4     (/±      ·   4290288
@$GPGGA,020415.00,4336.
#59411,N,07936.64845,W,
#2,6,2,141.69,M,-35,M,7
#,119*5F
!                4290338
EÿÈ     1/Y ·    4290496
@$GPGSA,A,3,30,,,25,,20
#,,14,,06,,01,02.8,02.1
#,02.0*0D
!                4290417
Eÿtr    /F    4290687
Eÿkø/ à ·
   4290893
Eÿh/lA ·
   4291101
Eÿ2     A/5Ñ ·   4291293
@$GPGGA,020416.00,4336.
#59420,N,07936.64848,W,
#2,6,2,142.11,M,-35,M,4
#,119*5C
!                4291335
E
tsÝ3 ·   4291502
@$GPGSA,A,3,30,,,25,,20
#,,14,,06,,01,02.8,02.1
#,02.0*0D
!                4291414
Eÿ*, bŒ "Y   4291691
C building       4291793
E
# *å "V   4291900
E¸/D "C   4292299
```

Appendix B

B.1 Using the EM61MK2 with a GPS Receiver

The EM61MK2 program accepts input from GPS receiver that stream NMEA-0183 compatible data through their output port. The program uses two NMEA messages: GGA and GSA. The entire GGA message is used later by the DAT61MK2 program, while the GSA message is used only to display PDOP index on the logger screen.

The GPS system means (control device, receiver panel, or manufacturer software) must be used to set GPS receiver communication parameters, to specify frequency of GPS output, and number and type of NMEA messages sent by the GPS system output port. Any GPS system can send various NMEA messages. **It is important to select only two messages (GGA and GSA) that are actually used by EM61MK2.** The program will accept any GPS string sent by the GPS receiver, however it uses time to process GPS data that is not being used. Therefore, selecting a larger number of NMEA messages for GPS output will result in slower data acquisition of EM61MK2. Normally, the EM61MK2 running in Allegro CX logger uses less than 100 ms to process and record GPS data from two NMEA messages, GGA and GSA.

Only message GGA is necessary to position EM61MK2 data. If message GSA is not available in a particular system, the EM61MK2 will function and record position data based on GGA message. Lack of GSA message will result in PDOP index displayed as Not Available (N/A) on the logger display. Using message GGA alone will also result in slightly faster operation of the program. The speed can be further improved by setting higher Baud Rate (if it is supported by the employed GPS receiver) in Set GPS Port menu.

The EM61MK2 dedicates one line of the display to show GPS status. A label **DGPS** (Differential Global Positioning System) that GPS readings are differentially corrected in real time Label **AGPS** (Autonomous Global Positioning System) indicates lack of differential correction. On the right side of the **POS** a label a slash character is displayed. This slash alternates between forward and back slash with the frequency of GPS update rate (usually 1 second intervals). If the slash is not moving for longer period of time it means that GPS system is not working or that it is not connected to the field computer. Number of recorded GPS positions are displayed on the right side of the alternating slash following # sign. This number is updated only in the logging mode, when the data are recorded. (In Stand By mode or during Monitoring only the alternating slash, and updated values of PDOP and number of tracked satellites, indicate presence of GPS input).

Two more GPS parameters are displayed on the logger screen. These are index PDOP shown by label **PDOP** and number of tracked satellites represented by label **Sat**. The index called PDOP (Position Dilution of Precision) measures the strength of satellite coverage for a given area. PDOP is affected by the number of satellites visible and their relative positions in the sky. The smaller the number of PDOP the stronger the satellite coverage is. When there are more than 5 satellites widely spaced visible, the PDOP is 4 or less. However, when there are less satellites visible, or they are unevenly spaced in the sky, PDOP values can be 6 or higher. In most cases, the PDOP in an open sky is less than 3, and most accuracies given for many GPS systems are given for this norm. Refer to GPS documentation and literature for more information related to error sources of GPS positioning.

B.2 Description of GGA and GSA Data Messages

GGA Data Message

The GGA message contains the GPS position information and it is the most widely used NMEA data message. This message takes the following form:

$GPGGA,hhmmss.ss,ddmm.mmmmm,s,dddmm.mmmmm,s,n,qq,pp.p,saaaaa.aa,u, ±xxxx.x,M,sss,aaaa*cc<CR><LF>

Definition of GGA message component:

hhmmss.ss	UTC time in hours, minutes, seconds of the GPS position
ddmm.mmmmm	Latitude in degrees, minutes, and decimal minutes
s	s=N or s=S, for North and South latitude
dddmm.mmmmm	Longitude in degrees, minutes, and decimal minutes
s	s=E or s=W, for East and West longitude
n	Quality indicator, 0 = no position, 1 = raw, no differentially corrected position, 2 = differentially corrected position, 9 = position computed using almanac information
qq	Number of satellites used in position computation
pp.p	HDOP = 0.0 to 99.9
saaaaa.aa	Antenna altitude
u	Altitude units, M=meters
±xxxx.x	Geoidal separation (requires geoidal height option)
M	Geoidal separation units, M = meters
sss	Age of differential corrections in seconds
aaaa	Base station identification
***cc**	Checksum
<CR><LF>	Carriage return and Line feed

GSA Data Message

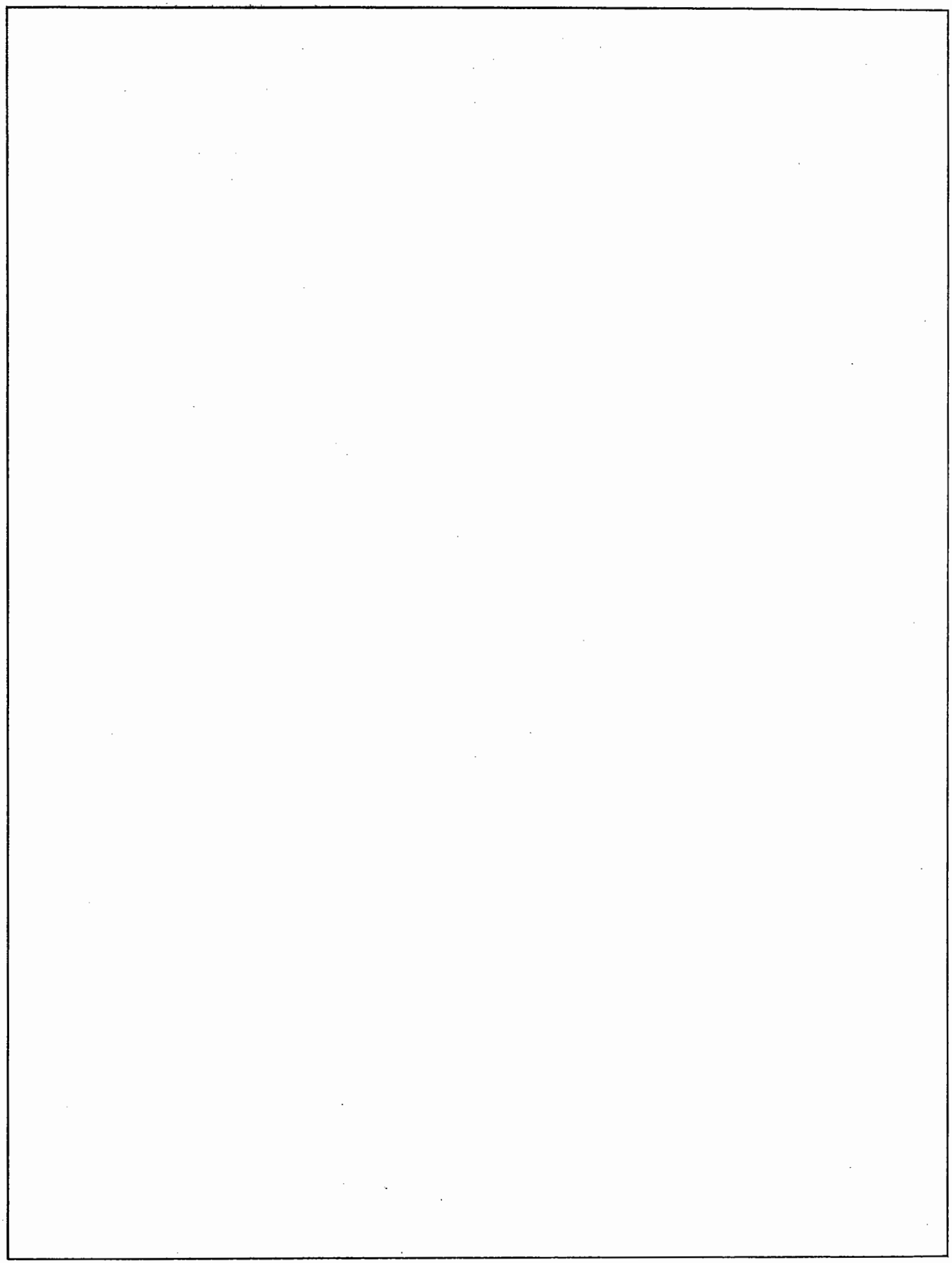
The GSA message contains active satellites and PDOP value. The GSA message is given in the following form:

$GPGSA,c1,d1,d2,d3,d4,d5,d6,d7,d8,d9,d10,d11,d12,d13,f1,f2,f3*cc<CR><LF>

Definition of GSA message components:

c1	Mode, M = manual, A = automatic
d1	Mode, 2 = 2D, 3 = 3D
d2-d13	Satellites used in position computation (range 0 to 32)
f1	PDOP (range 0 to 99.9)
f2	HDOP (range 0 to 99.9)
f3	VDOP (range 0 to 99.9)
***cc**	Checksum
<CR><LF>	Carriage return and Line Feed

C. SURVEY PROCEDURE



C. SURVEY PROCEDURE

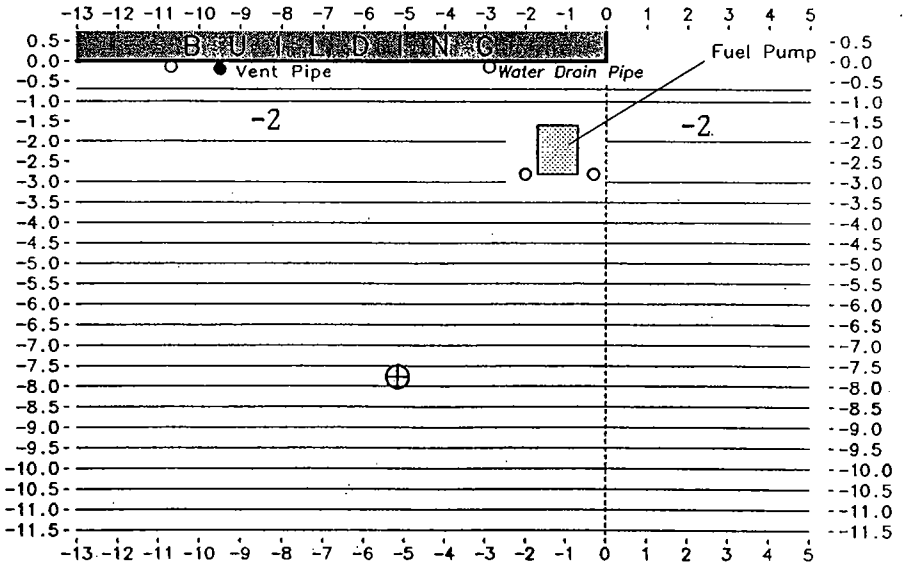
1. Survey Layout

A few minutes spent on the survey planning can save many hours during the preparation of data for mapping and interpretation. The survey reference point and reference line should be slected according to the site geometry and anticipated map layout. The survey lines should be parallel with either horizontal (**x**) axis or vertically (**y**) axis, regardless of the compass direction of the site.

If the direction of the expected target is known, chose the one (**x** or **y**) that is closer to being perpendicular to the targets longer dimension. For example, if you are looking for buried pipes, survey lines should be perpendicular to the pipe.

An exception to the above is when an expected target is parallel and close to a building, fence or wall. In such a case, lines should be parallel to the building (wall, fence) in order to produce a more continuous line across the anomaly. Otherwise, if the lines direction is perpendicular to the building a small error in the start and end of lines, that happen to be near the anomaly, will distort the pictures of the target.

In the case that target position or shape is not known, the most optimum line direction is the one parallel with the site's longest dimension. Once the line direction is selected, the labelling of lines should be done carefully. During the field operation direction, choice of negative and positive increments and start stations for each line should be entered according to the chosen geometry. Since the polycorder program records data only in one dimension (along the profile line) it is very helpful, and should be standard procedure, to use co-ordinates value in the line name. If for example, line co-ordinate is 10 (**x** or **y**), the line name should be labelled 10, or in the other example if the line adjacent to the zero line is separated 1 meter from it, this line should be labelled as 1.



The reference line (zero line) should go through reference point (0,0). If the lines are parallel with **x** axis, lines above the reference line are labelled as positive and lines below the reference line should be labelled as negative. If the lines are vertical (parallel with the **y** axis), lines to the right of the reference line are labelled positive and those to the left negative.

If the line is broken in several parts, different segments of this line should be labelled with the same name but a different start station.

2. Survey Line Spacing

The EM61 is an extremely high lateral resolution metal detector, and in comparison with some other metal detectors, especially with magnetometers, is more suitable for work in dense industrial environment, in the vicinity of buildinigs, fences, power lines and other sources of interferences. This advantage however leads to requirement of relatively fine spacing between the survey lines. It is a known fact that the higher number of data per unit area leads to easier and more accurate interpretation of data. This is especially true in case of environmental geophysics, dealing often with a large amount of anomalies distributed within relatively small site. The optimal separation between survey lines is 1 m (or 3 feet) and should not exceed 2 m (or 6 feet). In the case when 2 m spacing is used, large buried metallic targets will be detected, but the smaller near surface targets could be missed. In this case it is recommended that the operator monitors collected readings and in more complicated areas additional lines are added. For small sites with very high target density 0.5 m line apacing is sometimes used.

3. Survey Station Spacing (Recording Interval)

As pointed out earlier, EM61 is an extremely high lateral resolution instrument, meaning that it has capabilities to resolve closely spaced anomalies. To take full advantage of its resolution power, it it recommended that the station (recording) interval is in the range of 0.2 m (8"). Note that if the odometer mounted on the trailer wheel is used for recording, the interval is fixed at 0.193 meters or 0.63 feet.

4. Control of Recording and Instrument Position

The control of recording and instrument position along the survey line can be achieved by three different methods: odometer mode, auto mode and manual mode. Description of each mode follows:

4.1 Odometer Mode

Recording intervals and, therefore, recorded instrument position on the survey line is controlled by odometer/counter mounted on the trailer wheel. Triggering interval (increment) is fixed (it cannot by changed by operator) and it is nominally 0.193 meters or 0.63 feet. Two main factors can affect accuracy of increments: condition of the wheel tires (air pressure in the tire) and condition of test area surface. The larger effect of two is normally as a result of surface condition like: stones, tall grass, concrete curbs, etc.

The operator can easily determine increments for most conditions by surveying a test line of known length (approximately same length as survey lines) and then enter more accurate increments in the polycorder program.

In most cases however, the length of the survey line is known and the value for the increment of the wheel counter can be adjusted later during the processing of the data. For this reason it is always useful to record (e.g. in the field book) the end station of each survey line. If the test for the wheel counter is not performed in the field, the optimum value that should be entered in the logger is 0.193 meters (or 0.63 feet). It is recommended that while surveying longer lines a fiducial marker is used at the known intervals approximately 20 m (or 50 feet) apart. Stations with recorded markers can be easily positioned using program DAT61. This procedure will greatly improve accuracy of the survey.

4.2 Auto Mode

The auto mode of recording is normally performed if the trailer mode is either not available or not practical to use. In this mode data is collected at the time interval specified by the operator. The accuracy of the instrument positioning will depend mainly on the ability of the operator to walk at the constant speed. It should be noted that the speed of surveying should not exceed 1 m/s (or 3 feet/s). Since the recommended station interval is about 0.2 meters and with typical speed of 0.6 to 0.4 m/s, the recording rate in auto mode should be set to 2 to 3 records per second. The use of the fiducial marker is highly recommended if the auto mode recording is used. The marker should be used at the controlled intervals 5 to 10 meters (15 to 30 feet) apart.

4.3 Manual Mode

Manual mode of operation is used in the case, similar to auto mode, when the wheel mode of operation is either not available or, due to the difficult terrain, not practical to use. This mode is more labour intensive and slower but more accurate than the auto mode. In this mode of recording operator marks the survey lines, most conveniently by layinig measuring tape on the ground along the survey line, and records data by pushing recording button at the appropriate stations. As in the auto mode, recommended station intervals should be between 0.2 to 0.3 meters (8" to 12").

D. DATA PRESENTATION

The EM61 data is characterized by very high spatial resolution, high anomaly gradients (large change of response in the short spatial interval) and very high dynamic range of readings (response can range from 0.2 mV to 13 000 mV). As a consequence processing and presentation of EM61 data requires special consideration in order to obtain full advantage of the technique.

There are two types of basic presentation of EM61 data; profile form and contour maps. The following is a list and some examples of EM61 data with the several types of common mode of presentation.

1. Data Presented in Profile Form

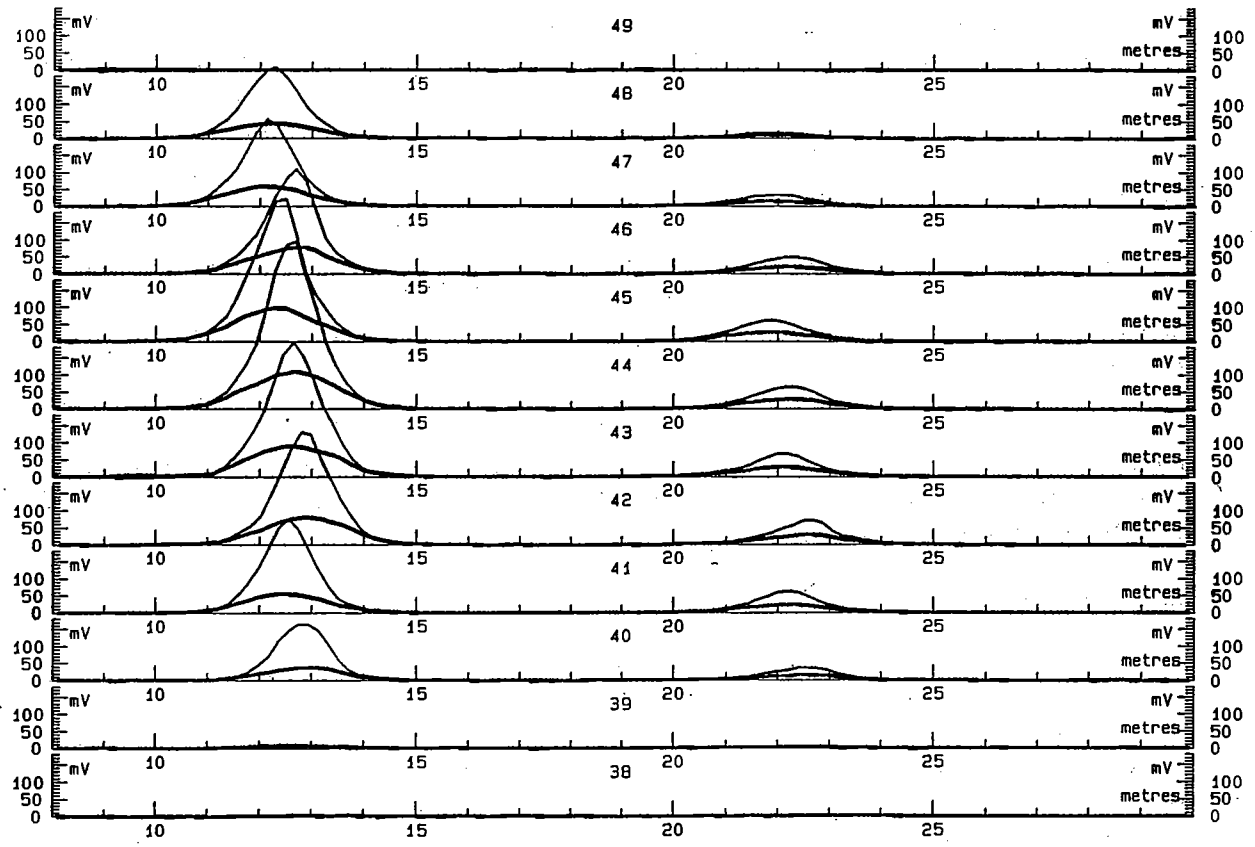


Figure 4

1.1 Comments Regarding the Presentation of Data in Profile Form

When looking for deeper targets that produce small amplitude (several tens of mV), the most optimum scale is the one that produces visible noise level, (typically 2 - 3mV for channel T and 1mV for channel 3. Due to the very large dynamic range of EM61 response, it is sometimes necessary to plot data at two different scales: first based on the maximum amplitude, and second based on the resolution and data noise level, and letting higher amplitude response to saturate.

2. Data Presentation in the Contouring Form

2.1 Samples of Black and White Contour Maps (Figure 5)

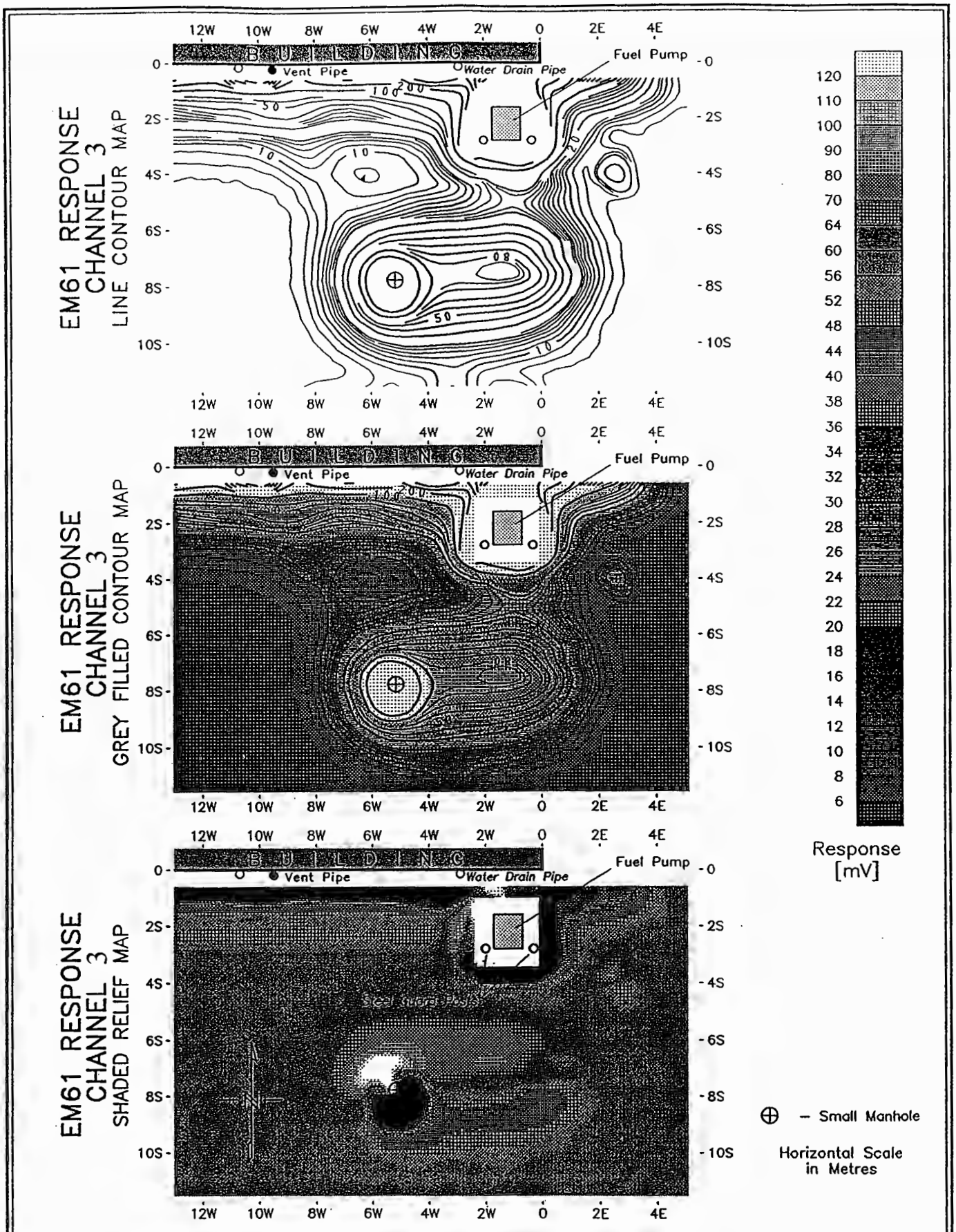
a. Line contour map
b. Gray filled line contour map
c. Shaded relief contour map

2.2 Samples of Colour Contour Maps (Figure 6)

a. Colour filled contour map

b. Colour filled contours with shaded relief map

c. Colour shaded relief map



GEONICS EM61 SURVEY OF A SITE WITH AN UNDERGROUND STORAGE TANK

Geomar Geophysics Ltd.

Figure 5

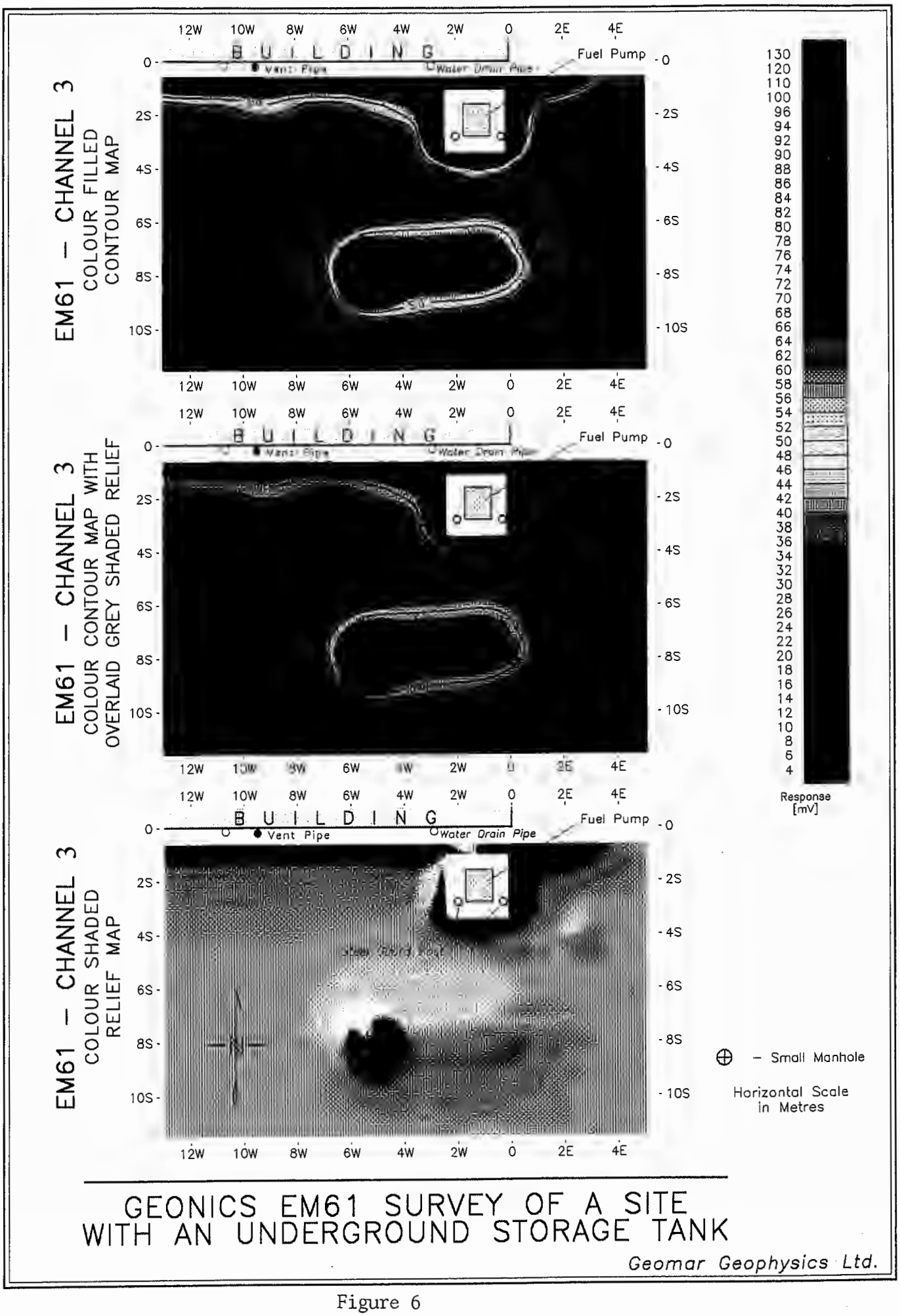

EM61 – CHANNEL 3
COLOUR FILLED
CONTOUR MAP
EM61 – CHANNEL 3
COLOUR CONTOUR MAP WITH
OVERLAID GREY SHADED RELIEF
EM61 – CHANNEL 3
COLOUR SHADED
RELIEF MAP
BUILDING
Vent Pipe
Water Drain Pipe
Fuel Pump
12W 10W 8W 6W 4W 2W 0 2E 4E
0 2S 4S 6S 8S 10S
130 120 110 100 96 94 92 90 88 86 84 82 80 78 76 74 72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4
Response [mV]
⊕ – Small Manhole
Horizontal Scale in Metres
GEONICS EM61 SURVEY OF A SITE
WITH AN UNDERGROUND STORAGE TANK
Geomar Geophysics Ltd.

Figure 6

2.3 Comments Regarding the Presentation of Data in Contouring Form

As mentioned earlier, the typical separation between data points during the recording is 0.19 m (0.62') along the survey line, and 1 m (3') across the lines. The adequate grid cell size for contouring would be 0.2 to 0.25 m (0.65 to 0.8 feet). A contouring software usually has a specified maximum number of grid points that can be used for contouring (GEOSOFT Mapping Software has 120,000 grid points for the **Geonics** package). One should also calculate what is the maximum size of the survey area that can be plotted on one map. In most cases presenting more than 1 hectare (or 2 acres) on one sheet (up to B size) leads to some loss of information, unless software allowing large number of gridding points and larger sheet size is used.

During gridding procedure care should be taken which interpolation algorithm is used. Since the typical EM61 anomaly has relatively high gradient, the commonly uses cubic interpolation very often produces overshoots that generates visible ghost depressions on the map. This effect can be alleviated by using Akima spline available in GEOSOFT Mapping Software. Spline should be used along and across the direction of survey lines.

During selection of colour scale for map of the EM61 data, the default settings of contouring software uses extreme values from data set. One should note that in most cases important anomalies, originated by deeply buried objects, are of much lower amplitude (tens or hundreds of mV) than those originated by near surface targets (thousands of mV). Adjusting the colour scale to the lower portion of the data range and leaving saturated high amplitude anomalies (usually short spatially) will produce reasonable map.

E. DATA INTERPRETATION (Applies to D (Differential) mode only)

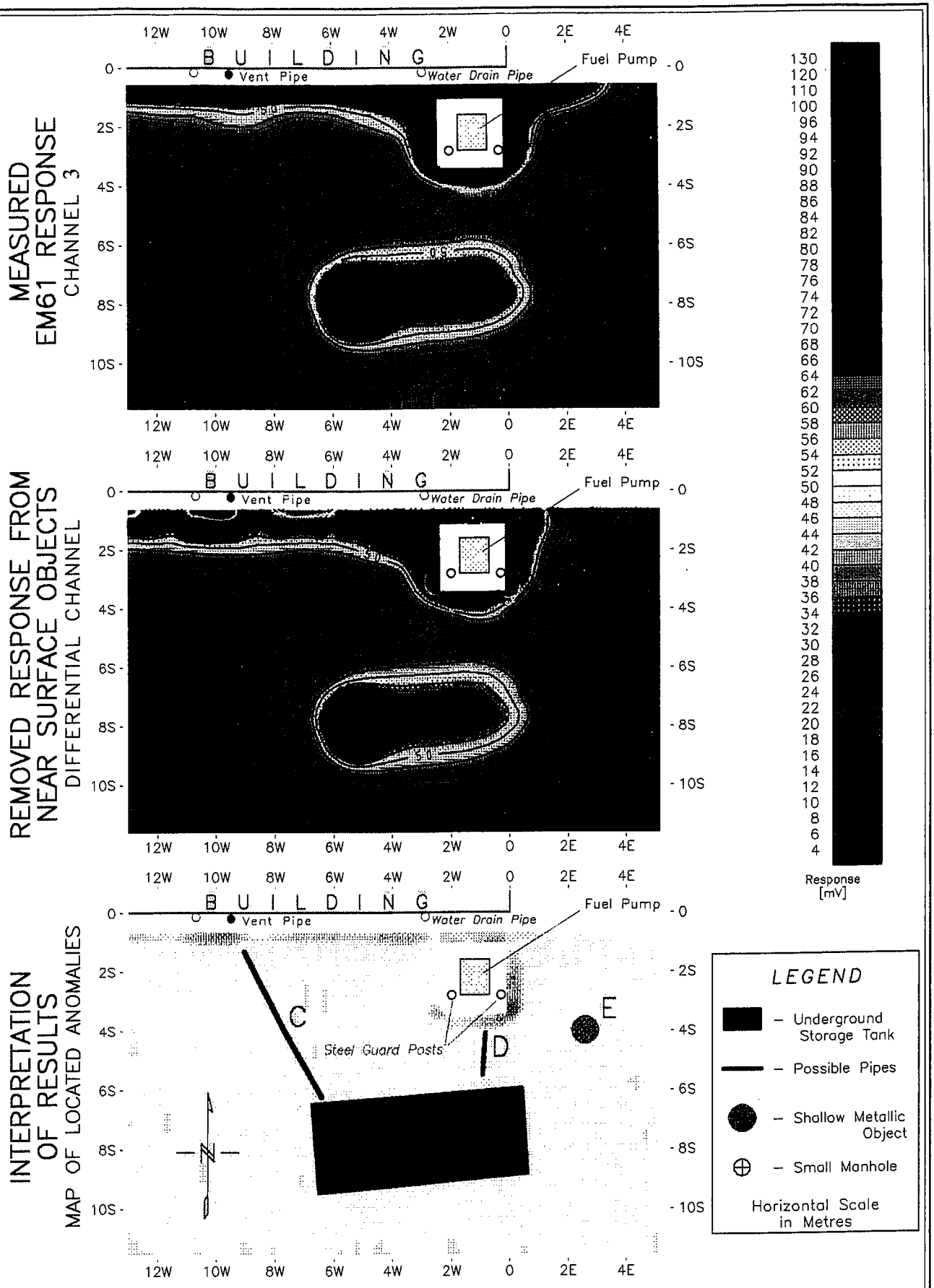
The EM61 is designed in such a way that it is possible not only to separate anomaly spatialy, but it is also possible under most conditions, to distinguish deeper targets from shallow ones. In addition, the unique two receiver coil system allows suppression of near surface targets that may mask response from deeper more important ones. This feature is very useful when the purpose of the survey is to locate deeper targets, like underground storage tanks or drums, in presence of shallow near surface metallic objects (manhole cover or metal scrap).

Further benefit of two receiver coils is the ability of the system to reduce the effect of external noise as it will be described later.

1. Separation of Shallow and Deeper Targets
(Suppression of Near Surface Targets Response)

The two receiver coils antenna system used in EM61 is very helpful in recognition of near surface object from deeper targets.

Since the amplitude of response is highly depended on the distance between the coil assembly and target, small near surface anomalies will very often produce a response orders of magnitude larger than much bigger but deeper targets. This



GEONICS EM61 SURVEY OF A SITE WITH AN UNDERGROUND STORAGE TANK

Geomar Geophysics Ltd.

Figure 7

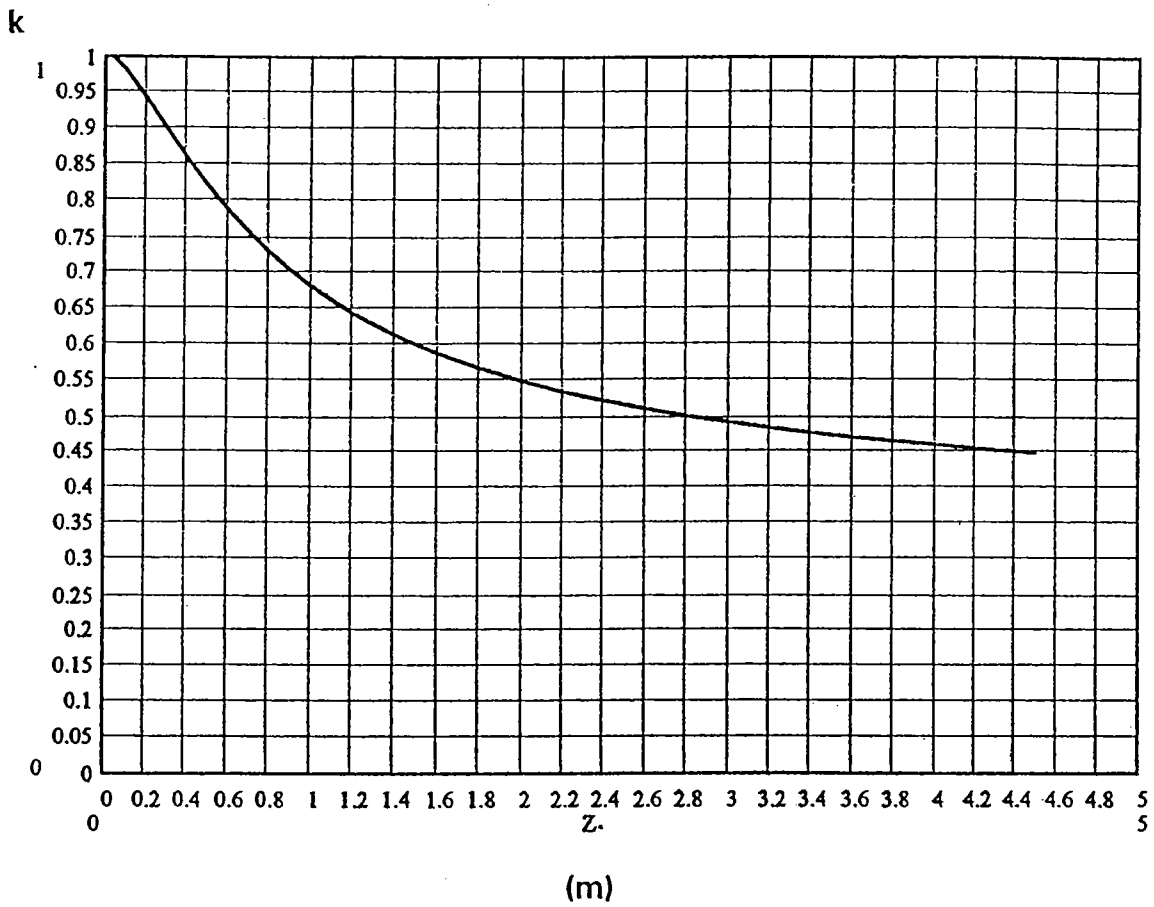

k
1
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2 2.2 2.4 2.6 2.8 3 3.2 3.4 3.6 3.8 4 4.2 4.4 4.6 4.8 5
0
Z.
5
(m)

Figure 8

masking effect from near surface material could be drastically reduced by using output of two coils and process them in the differential mode. In this case output from channel 3 is subtracted from channel T. Channel T represents data from top receiver coil, whereas channel 3 is data from coil closer to the ground. This calculation is automatically performed by EM61 DAT61 computer program.

The most common way of interpretation of EM61 data is by using channel 3 and differential channel data.

The differential channel is calculated by the program in the following way:

D = k CHT - CH3

where:

D is differential output in mV
CHT is output from top coil in mV
CH3 is output from bottom coil in mV - Channel 3
k is depth coefficient normally set to 1

It is possible to vary **k**, and adjust the depth at which the response will be suppressed the most. If **k** is selected to be 1, the response from targets right below the surface will be reduced the most. If the coefficient **k** is made smaller than 1, the deeper target will be suppressed more than shallow targets. In this case surface anomalies will have negative response in the differential channel.

It should be noted that the degree of cancellation will be affected by size, shape and depth of targets. The response from the targets with the small dimensions shaped like balls, shales or small plate-like targets parallel with the ground, is possible to reduce much more than response from larger 3 dimensional targets.

Figure 7 is an example of data presentation and interpretation using channel 3 and differential channel data. Channel 3 map (Figure 7a) contains information about all targets within the reach of EM61 system. This includes near surface and deeper targets response. On the other hand the differential channel map (Figure 7b) shows mostly deeper targets with removed or largely suppressed response from near surface material. For example, anomaly "E" on the right top corner of Figure 7a has disappeared on Figure 7b indicating a shallow target.

The Figure 7c shows interpretation based on channel 3 and differential channel data.

Locations of pipes C and D are based on the information from the profile plots, as well as from the "saddle" type of response on the channel 3 contour map.

Note that the negative values on the differential channel map are often associated with the metallic objects located above the surface, assuming that the depth coefficient of 1 is used (normal practice).

2. Calculation of Apparent Depth of Target

The EM61 computer program DAT61, version 1.3 or later, allows the user to estimate an approximate depth (apparent depth) of a target. This paramater is calculated on the basis of ratio of amplitude from channel T and channel 3 response. The apparent depth estimation is most accurate when the instrument is positioned over the center of buried target. (An additional reason from choosing fine spacing between the survey lines). In order to determine position of an anomaly, the peak response of the channel 3 profile should be examined along the survey line, as well as, on the neighbouring survey lines. By comparing responses of nearby lines and selecting anomaly maximum, it is normally easy to locate the position of the target. The apparent depth is determined at the highest point (peak) of the anomaly.

It should be noted that the calculation of depth is an approximation. The accuracy of estimation will depend on the relation between the line (station) and center of the target, the size and shape of target, as well as on the quality of data.

Depth estimation for the smaller ball shaped targets will be more accurate than the estimation for larger targets (like underground storage tanks or pipes). Depth for the larger targets will be normally overestimated, meaning that the anomaly will appear deeper than it actually is.

In order to improve depth estimation accuracy, especially for deeper targets with low response, it may be necessary to remove a small offset from the readings. Although each instrument prior to leaving the factory has outputs of both channels adjusted to read zero, it is possible that with time a small offset of several millivolts appears at the output(s). This effect could be recognized as a small non-zero shift in readings over the portion of the survey line that has no visible anomaly response. EM61 computer program DAT61 allows removal of such offset by shifting the whole line by a constant.

Figure 8 is an example of EM61 data from the site with buried ordnances. Line 531 is the line closest to the center of the targets (amplitude of response on this line is larger than response from adjacent lines 3 feet apart on each side). Vertical lines and associated numbers indicate selected targets and calculated depth in feet below the surface.

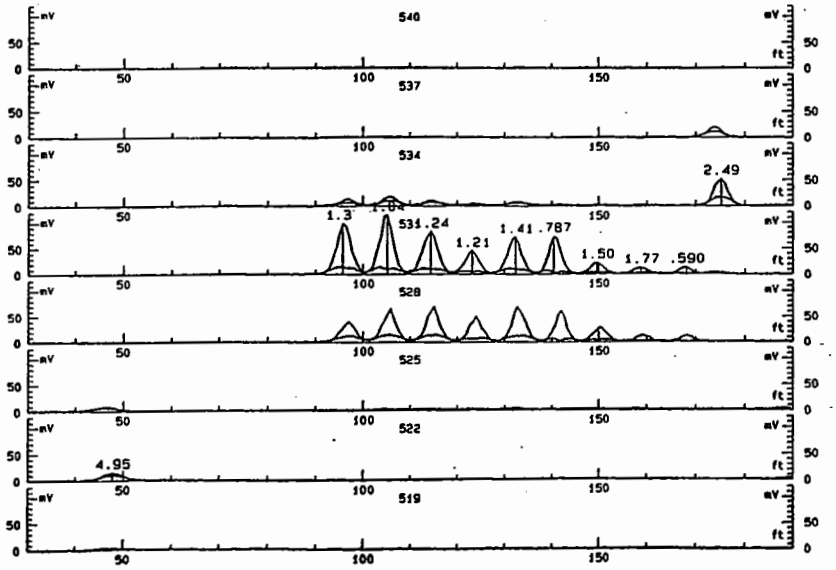


Figure 8

3. Reduction of External Noise
(Channel N)

The EM61 is designed to reject the influence of the external noise to a very high degree. Nevertheless, in some special cases where the sources of noise, especially power lines, are crossing the survey area or are very close by, the external electromagnetic noise may contaminate the survey data. In such a case the two receiver coils system could be used very effectively in filtering out this noise.

The reduction of the noise is based on the fact that each of the two receiver coils is receiving noise from the same source and by appropriate selection of the gain of each coil (channel) and subtracting outputs from channels, an order of magnitude reduction of noise could be achieved. A very small penalty in doing this is a negligible reduction of response from targets.

As described in section E.1 the differential channel is calculated by the software in the following way:

$$\mathbf{D = k\ CH\ T - CH\ 3}$$

By selecting the depth constant **k** to be 0.28, the channel T output is normalized to have the same "noise gain" as channel 3.

$$\mathbf{D_N = 0.28\ CH\ T - CHB\ 3 = - CHN}$$

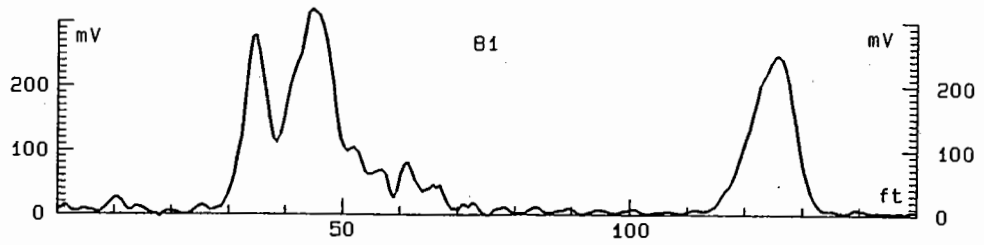
The differential channel automatically calculated with channel T normalized in this way, is presented as a new channel N. This channel will have target response very similar to the target response of channel 3 and in many cases drastically reduced noise level.

The example of the noise reduction on the actual data using the described technique is illustrated in Figure 9.

Figure 9a shows channel 3 profile from a survey site contaminated by the 60 Hz power line.

Figure 9b shows channel N (normalized differential channel) of the same survey line with the drastic reduction of the noise caused by the power line.

a)



b)

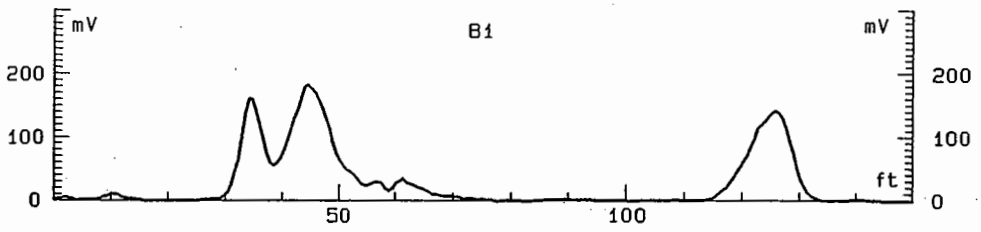


Figure 9

It should be noted that in the case when the differential channel with depth constant k=0.28 is used instead of channel N (automatic noise reduction normalization), the output will be inverted from the standard positive target response.

If the described noise reduction technique is used, and improvement of data quality is noticed, the new channel (channel N) normally replaces channel 3 during the interpretation. Note that the degree of noise reduction will depend on the noise source characteristics and will vary from site to site.

F. RESPONSE FROM SOME STANDARD TARGETS

In order to assist in planning and interpretation of EM61 survey, the following section contains information with the responses from some typical targets like: pipes, balls and 55 (US) gallon (208 l) steel drum.

The first set of graphs gives the response for each of two channels from the targets at the different depths below the EM61 coil assembly. This information can be used initially during the survey planning to assess in estimating the magnitude of response from known target at the specific depth of burial. Later, during the interpretation of the survey results, the same curves could be used to determine the depth of the target, providing that the characteristics of the target are known.

The curves are given separately for steel (or iron) targets, as well as for nonferrous metallic targets like aluminum or copper pipes and balls.

It should be noted that the targets at a specific site will have some of the parameters like: length, wall thickness, or in case of steel target magnetic susceptibility, different from one used to generate given graphs, but in general the response will not be significantly different. In the case of when graphs are used to determine the response from the pipes, the minimum length of pipe has to be over four meters, in order not to make significant error. The depth determination using graphs will be in general more accurate than the method of using apparent depth calculation described in Section E of this manual. Note that diameter of the pipes refer to the outside diameter of the pipe.

The point 3. of the section gives response from 55 (US) gallon steel drum in the vertical position at the different depth below the coil assembly. The response from a horizontal drum will be virtually the same.

The point 4. of this section gives an approximate depth of investigation for different standard targets based on the minimum signal response of 2 mV for the second channel. Since under the normal survey condition, the second channel noise is typically less than 0.5 mV, the threshold level of 2 mV is quite a reasonable value to use.

Note that the following graphs show response from various targets with (below surface) depth assuming the use of 1 x 1 m coils. With the 1 x 0.5 m coils (now standard size sensor) the response will be about 2.5 times higher for targets just below the surface and approximately the same for targets at the depth of 0.5 m and deeper.

As mentioned earlier (Section D), T is channel represent response from the top coil and CH 3 is the channel represent response from the bottom coil, 3rd gate.

Figure 10 illustrates measuring geometry used for measurements to generate supplied graphs.

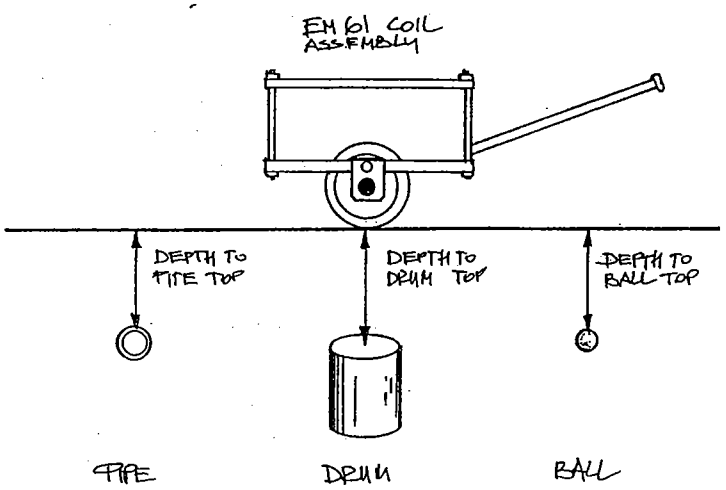
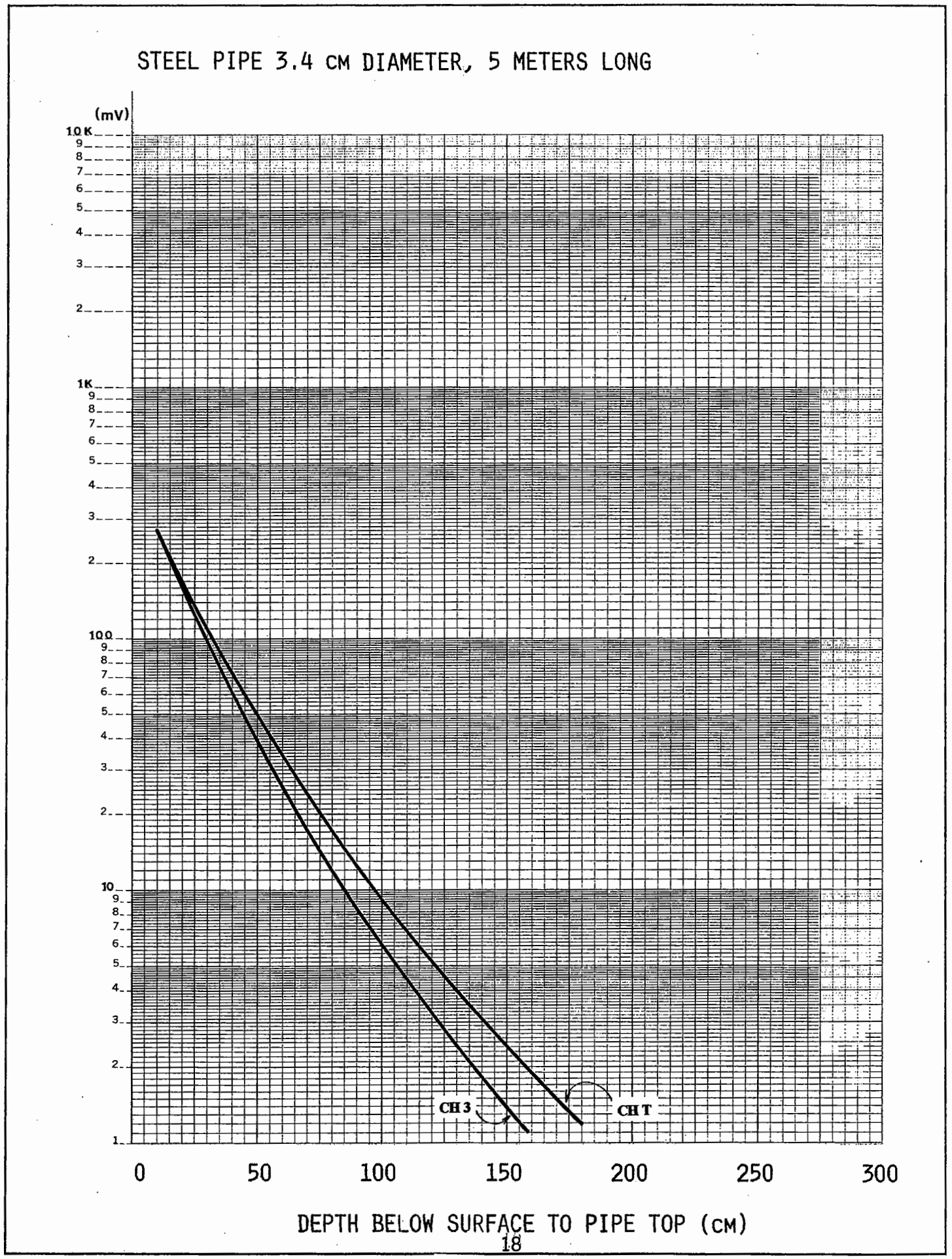


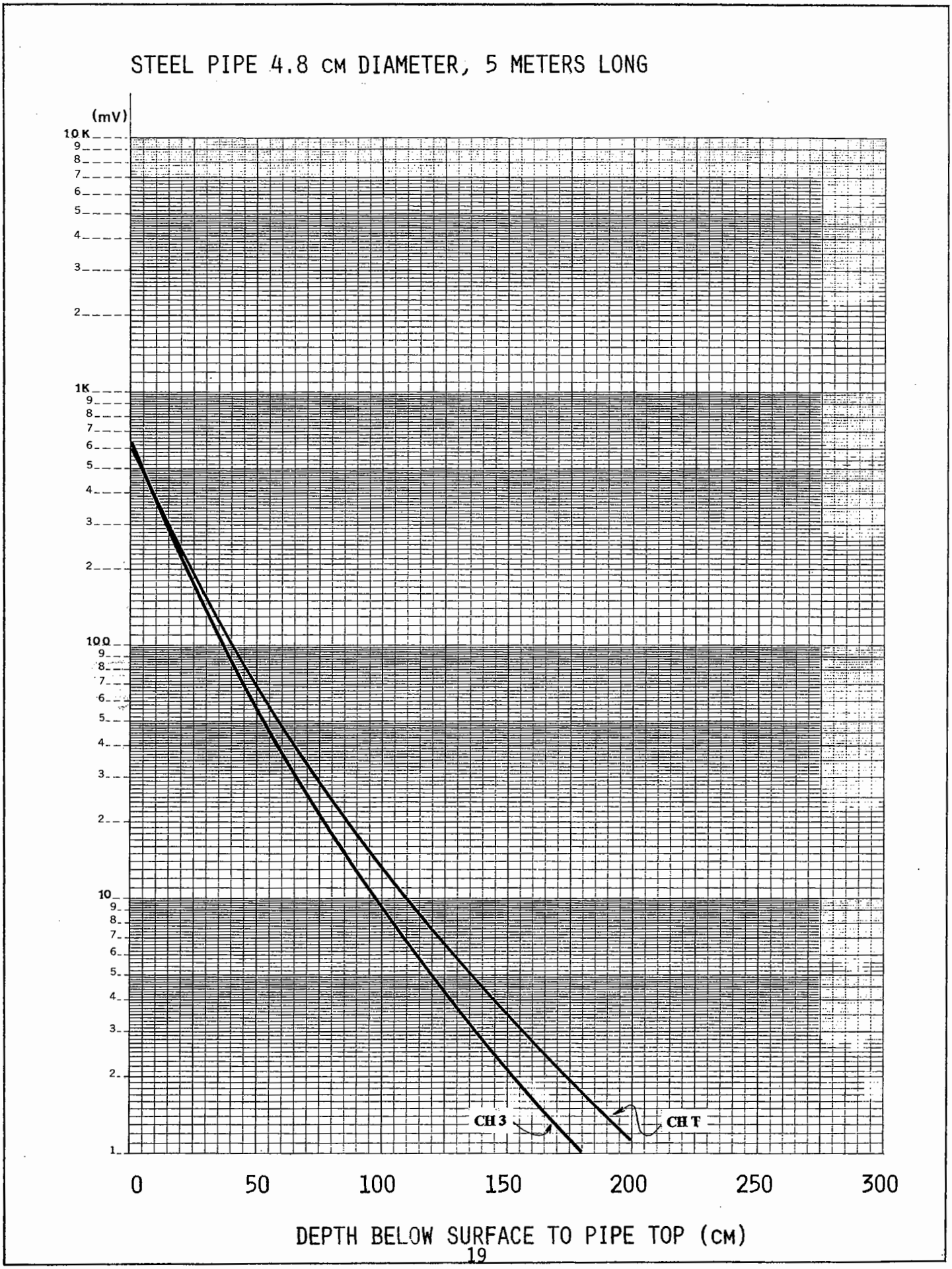
Figure 10

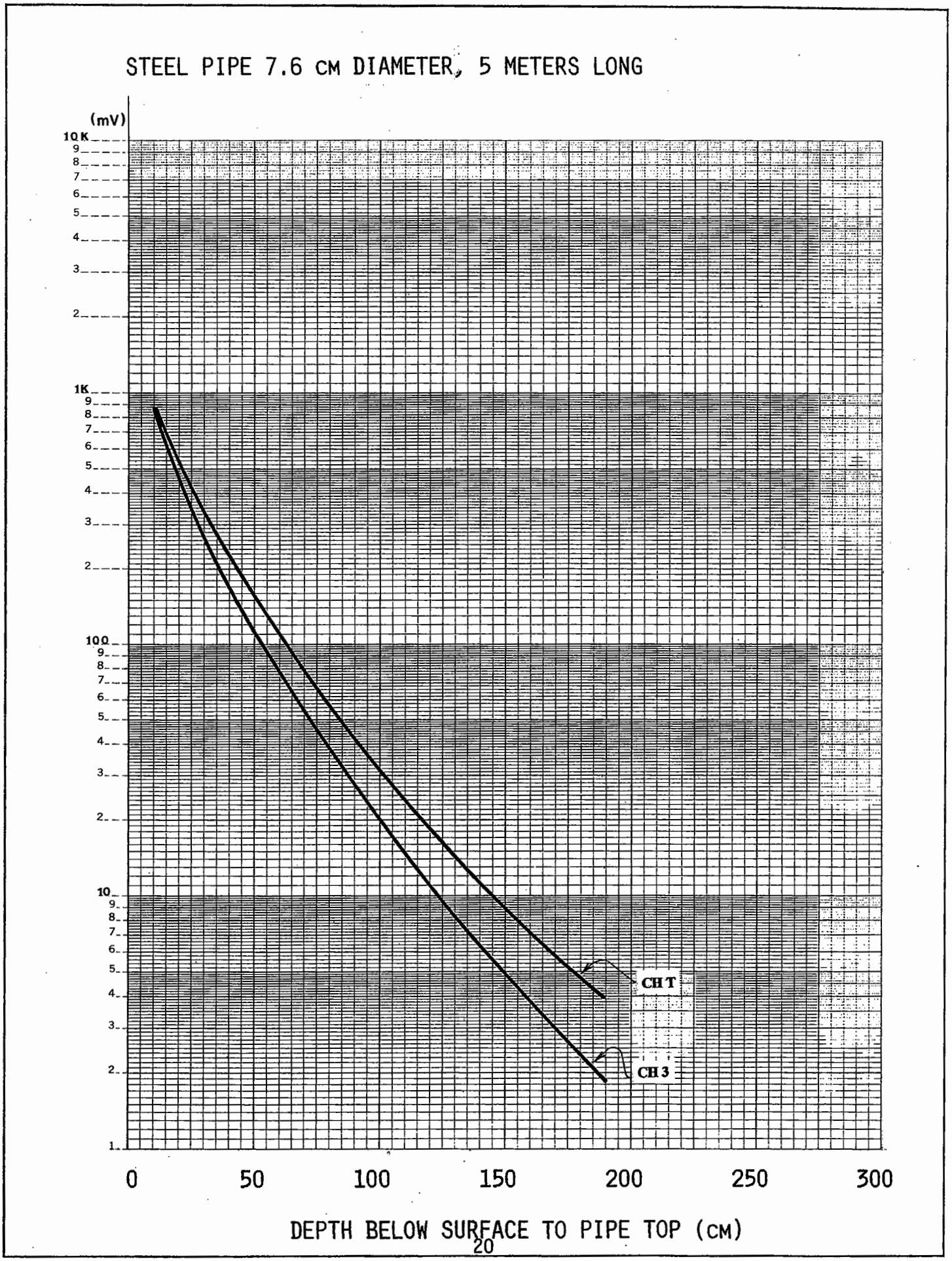
1. Pipe Response with Depth

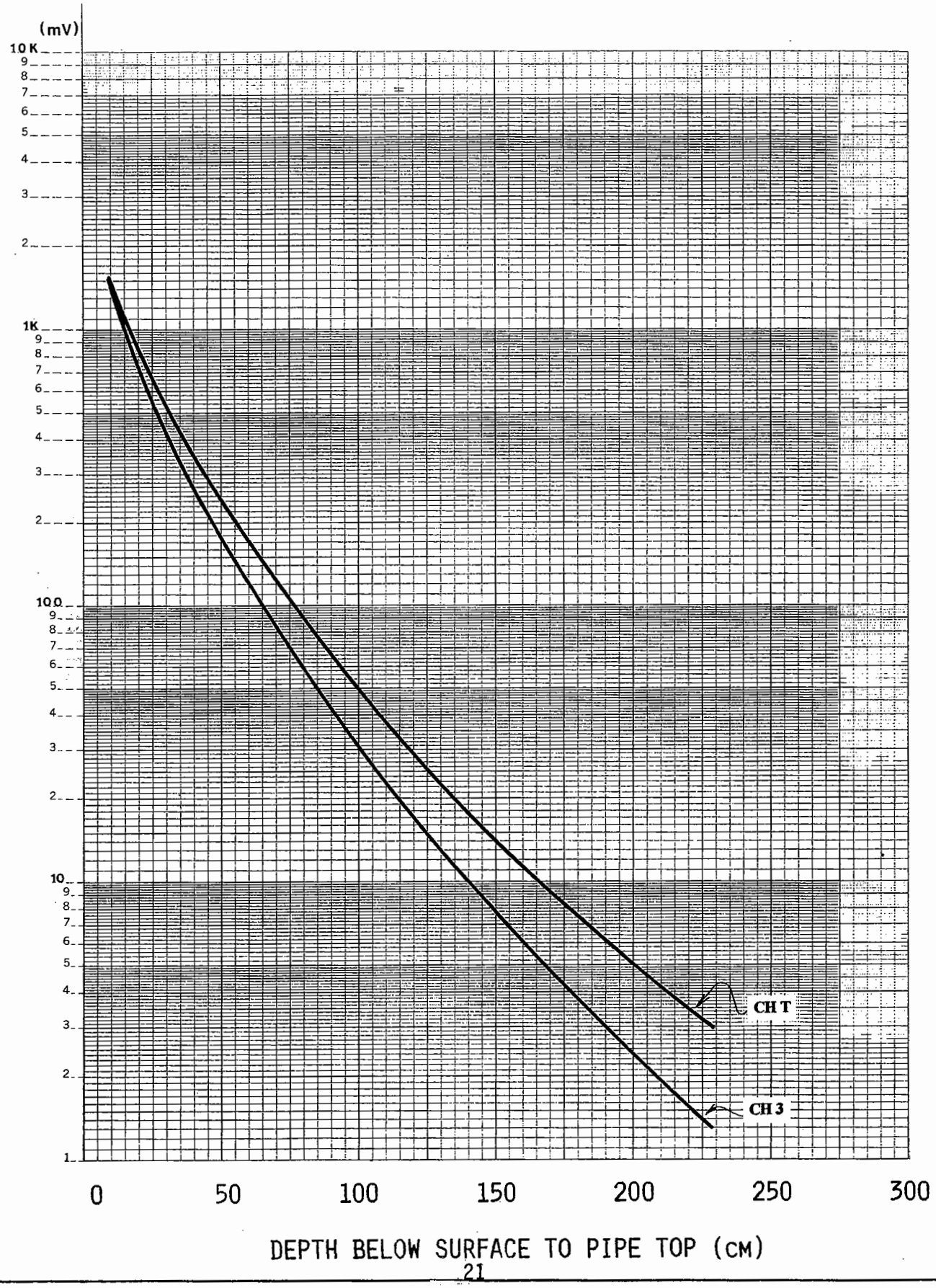
1.1 Ferrous (Steel, Iron) Pipes

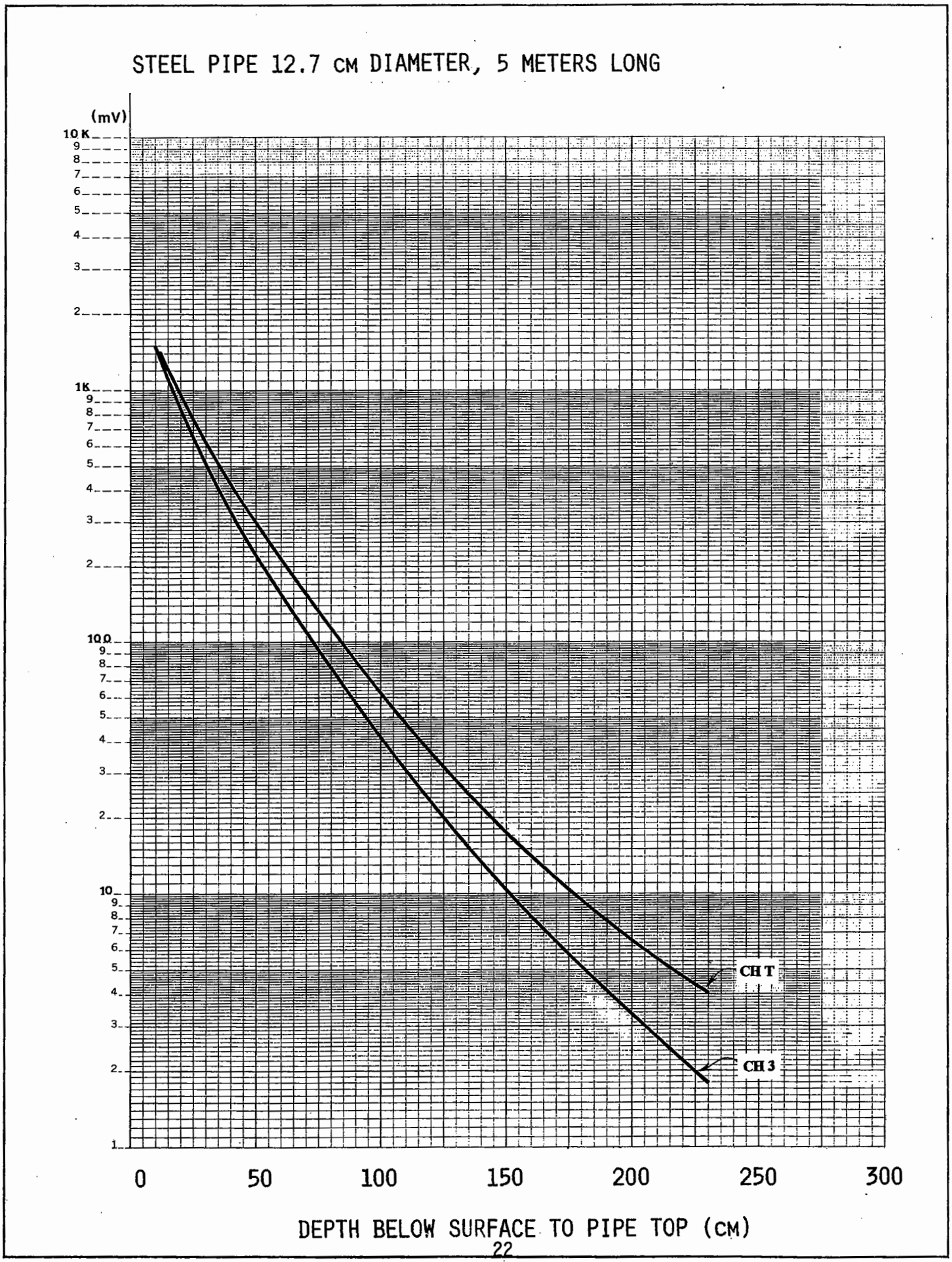
- Steel Pipe 3.4 cm Diameter, 5 Meters Long
- Steel Pipe 4.8 cm Diameter, 5 Meters Long
- Steel Pipe 7.6 cm Diameter, 5 Meters Long
- Steel Pipe 10 cm Diameter, 5 Meters Long
- Steel Pipe 12.7 cm Diamaeter, 5 Meters Long
- Steel Pipe 17 cm Diameter, 5 Meters Long
- Steel Pipe 20 cm Diamater, 5 Meters Long

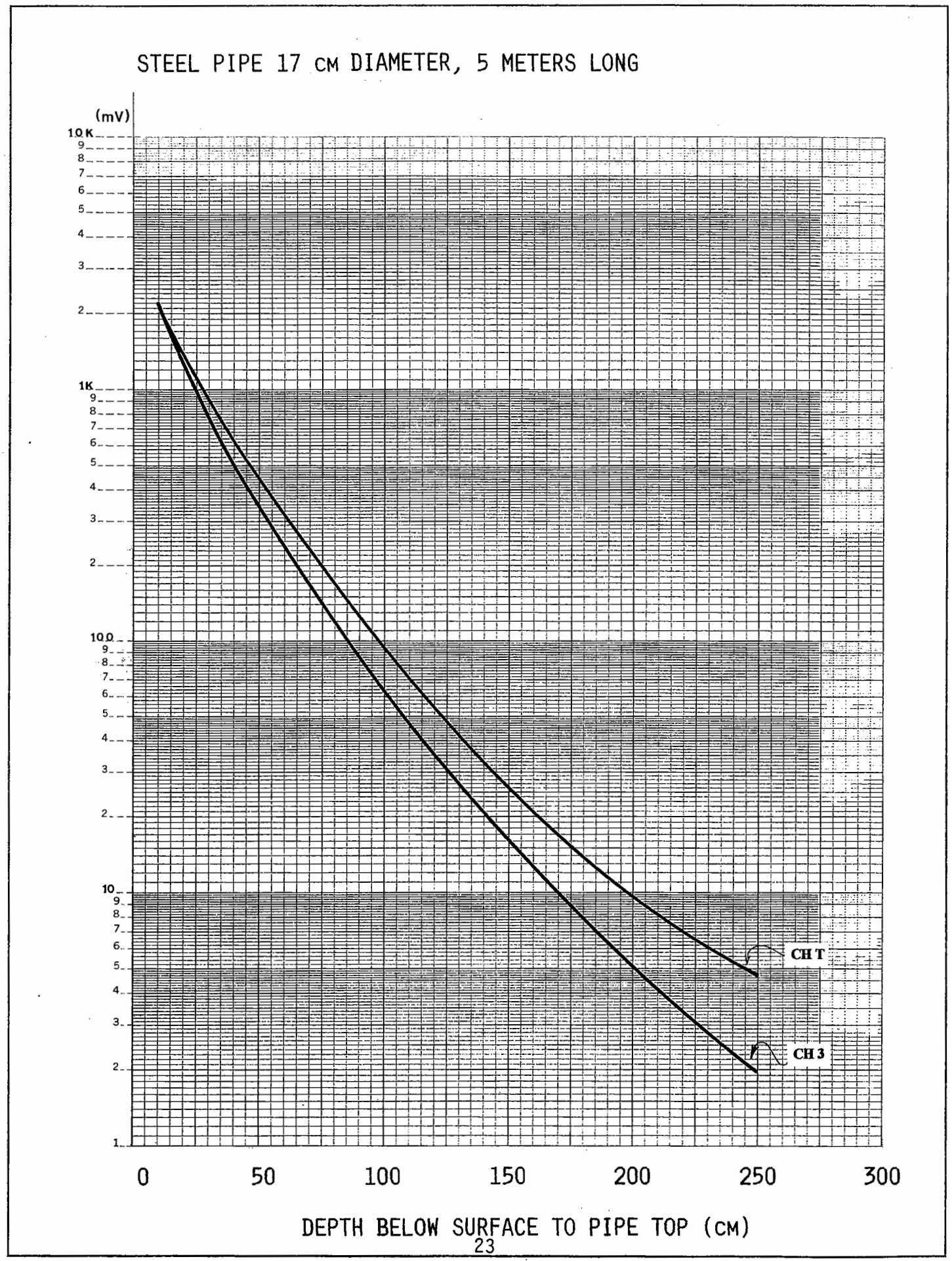

STEEL PIPE 3.4 CM DIAMETER, 5 METERS LONG
(mV)
10K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH 3
CH T
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (CM)

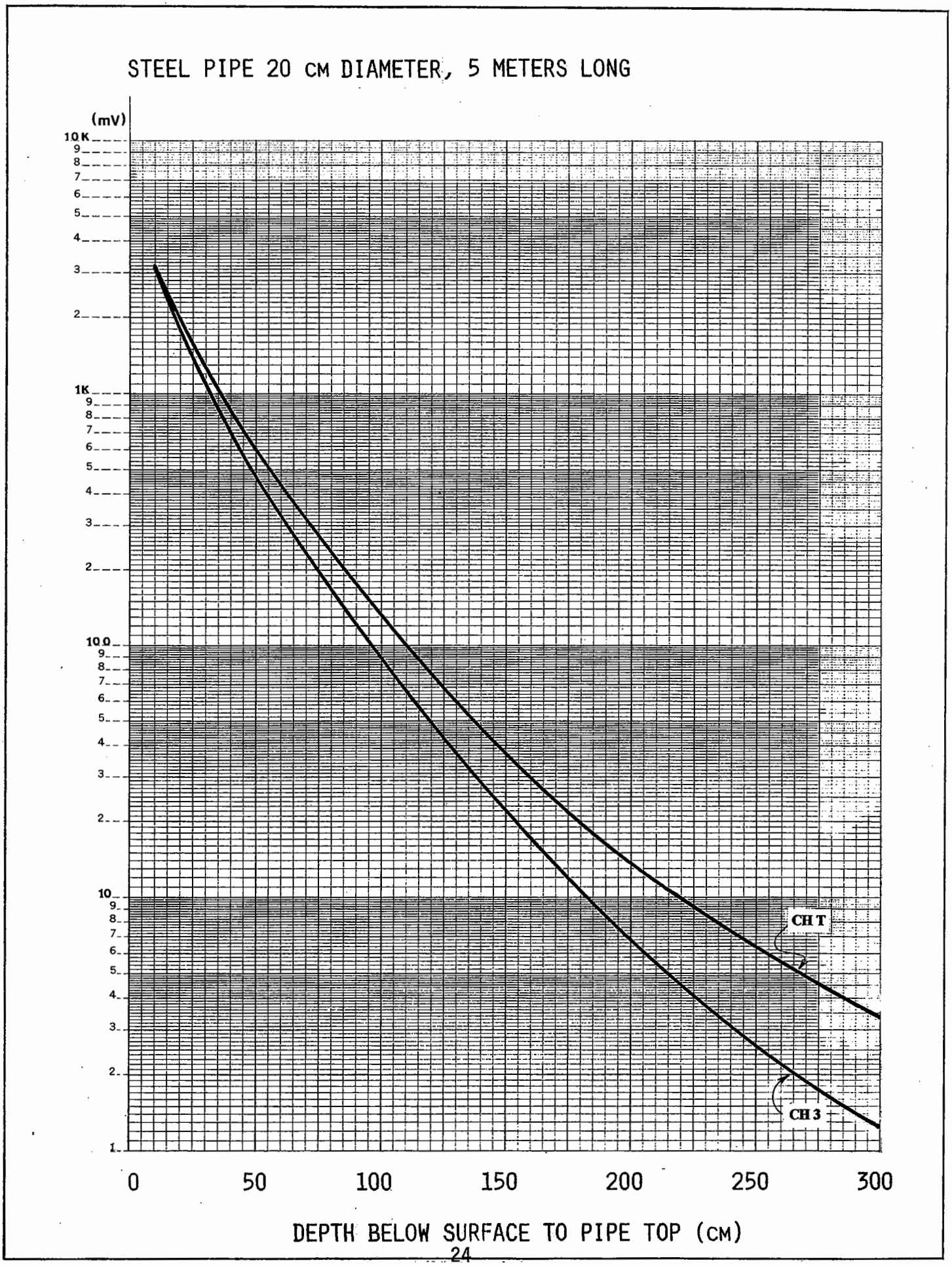

STEEL PIPE 4.8 CM DIAMETER, 5 METERS LONG
(mV)
10K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH 3
CH T
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (CM)


STEEL PIPE 7.6 cm DIAMETER, 5 METERS LONG
(mV)
10K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH T
CH 3
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (cm)


STEEL PIPE 10 cm DIAMETER, 5 METERS LONG
(mV)
10 K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH T
CH 3
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (cm)

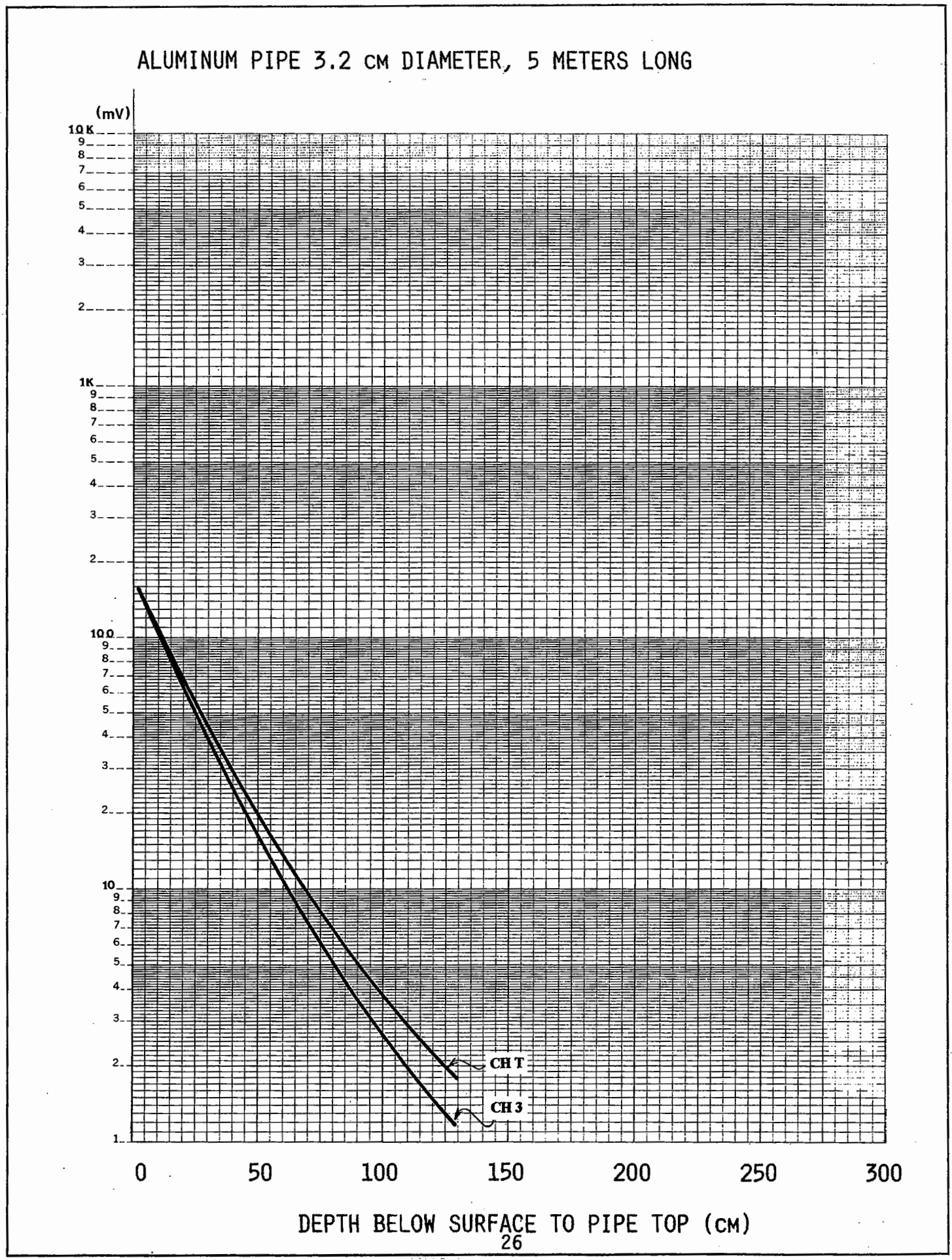

STEEL PIPE 12.7 cm DIAMETER, 5 METERS LONG
(mV)
10 K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH T
CH 3
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (cm)

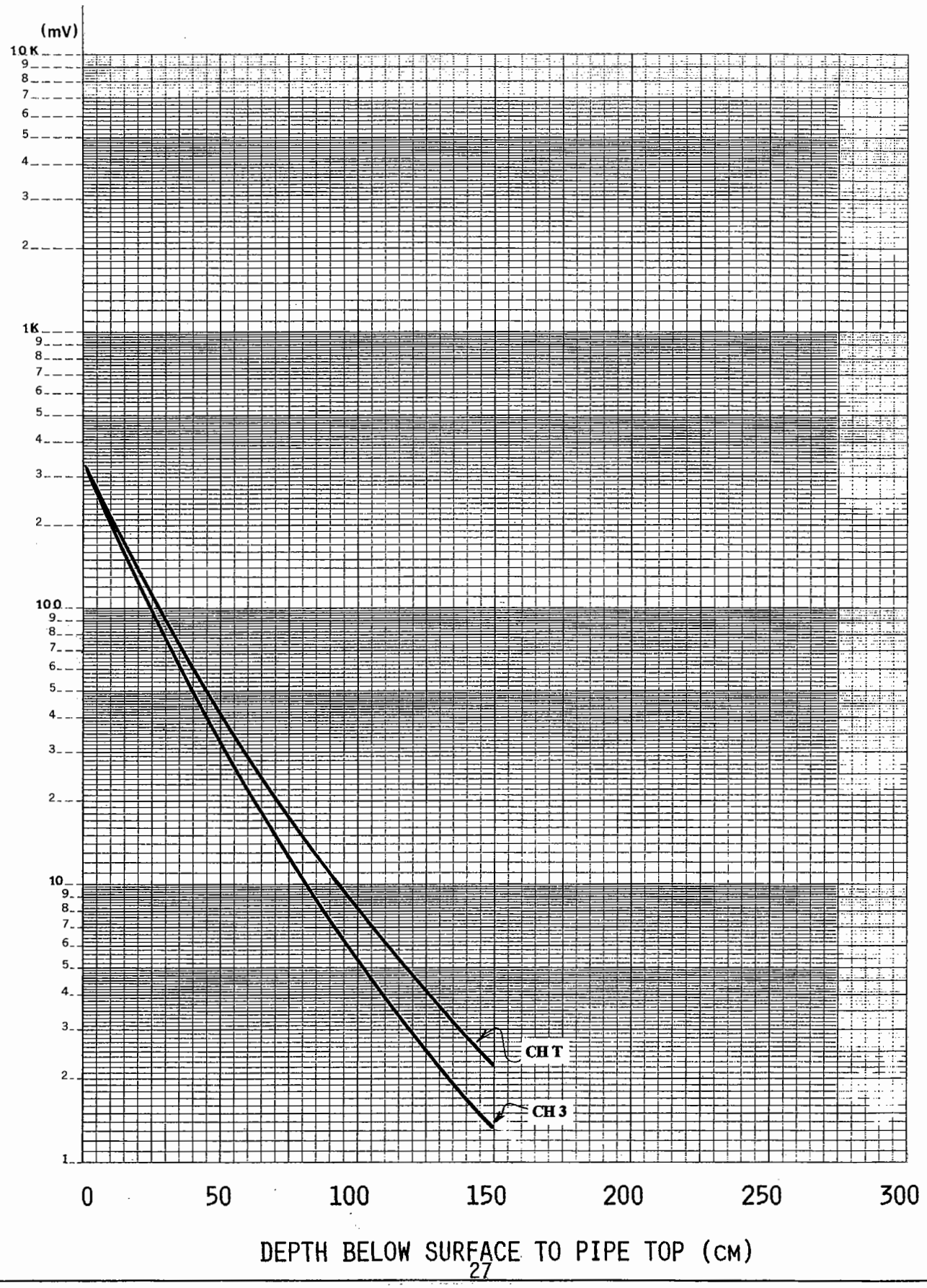

STEEL PIPE 17 CM DIAMETER, 5 METERS LONG
(mV)
10K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH T
CH 3
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (CM)

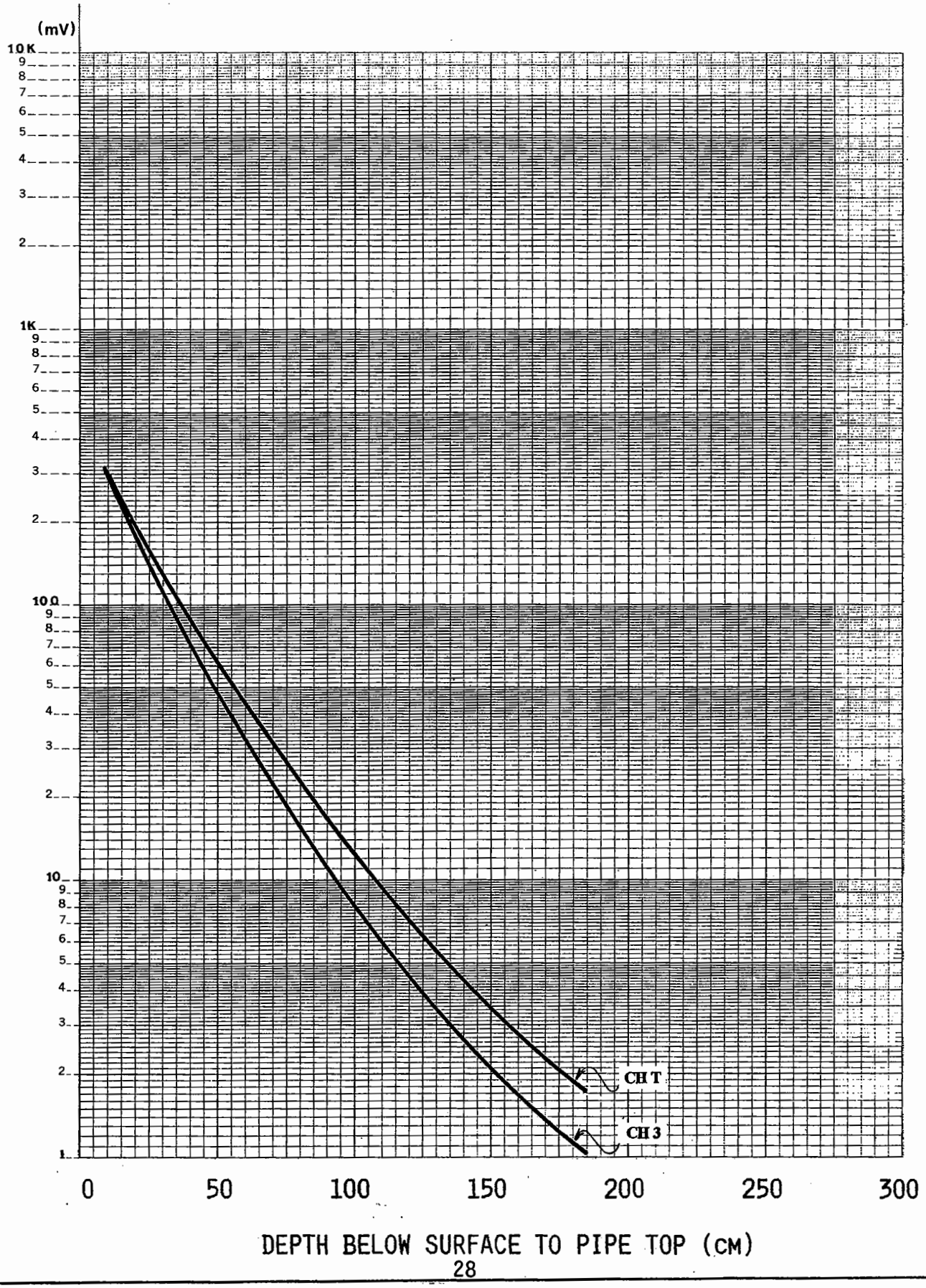

STEEL PIPE 20 CM DIAMETER, 5 METERS LONG
(mV)
10K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH T
CH 3
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (CM)

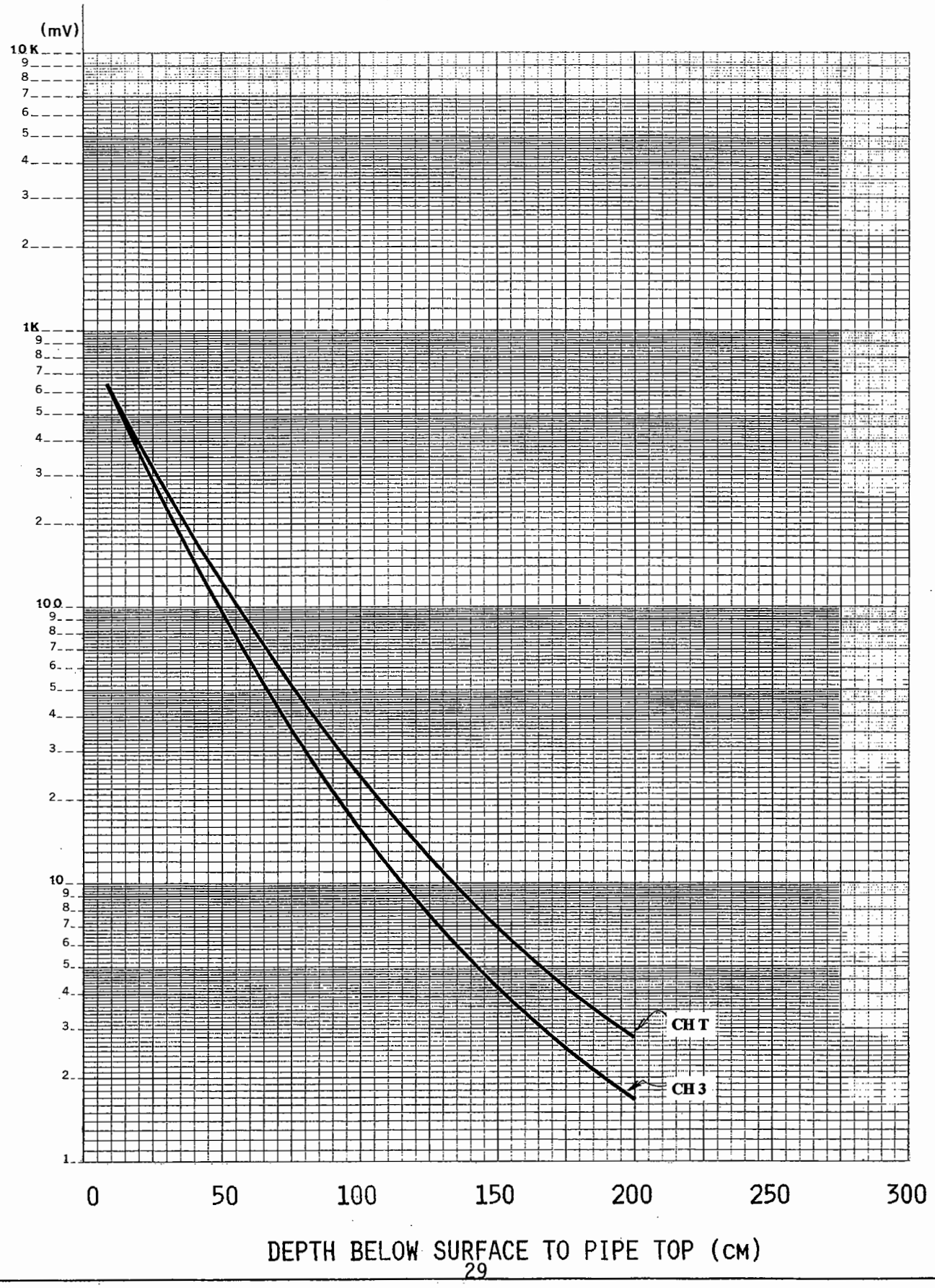
1.2 Nonferrous (Aluminum, Copper) Pipes

- Aluminum Pipe 3.2 cm Diameter, 5 Meters Long
- Aluminum Pipe 5.1 cm Diameter, 5 Meters Long
- Aluminum Pipe 10 cm Diameter, 5 Meters Long
- Aluminum Pipe 20.3 cm Diameter, 5 Meters Long


ALUMINUM PIPE 3.2 CM DIAMETER, 5 METERS LONG
(mV)
10K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH T
CH 3
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (CM)


ALUMINUM PIPE 5.1 CM DIAMETER, 5 METERS LONG
(mV)
10K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH T
CH 3
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (CM)

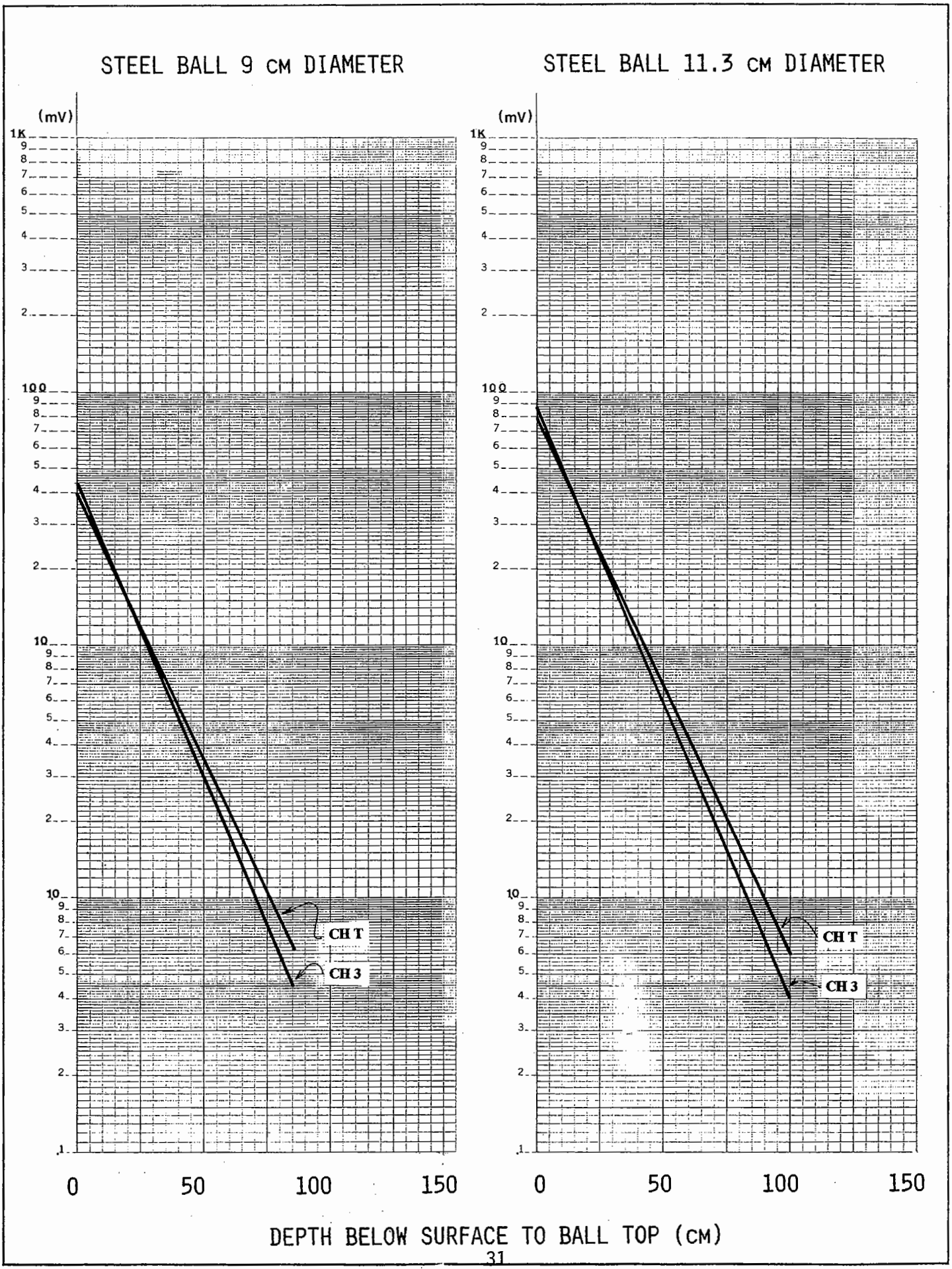

ALUMINUM PIPE 10 CM DIAMETER, 5 METERS LONG
(mV)
10K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH T
CH 3
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (CM)


ALUMINUM PIPE 20.3 cm DIAMETER, 5 METERS LONG
(mV)
10K
9
8
7
6
5
4
3
2
1K
9
8
7
6
5
4
3
2
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
CH T
CH 3
0
50
100
150
200
250
300
DEPTH BELOW SURFACE TO PIPE TOP (cm)

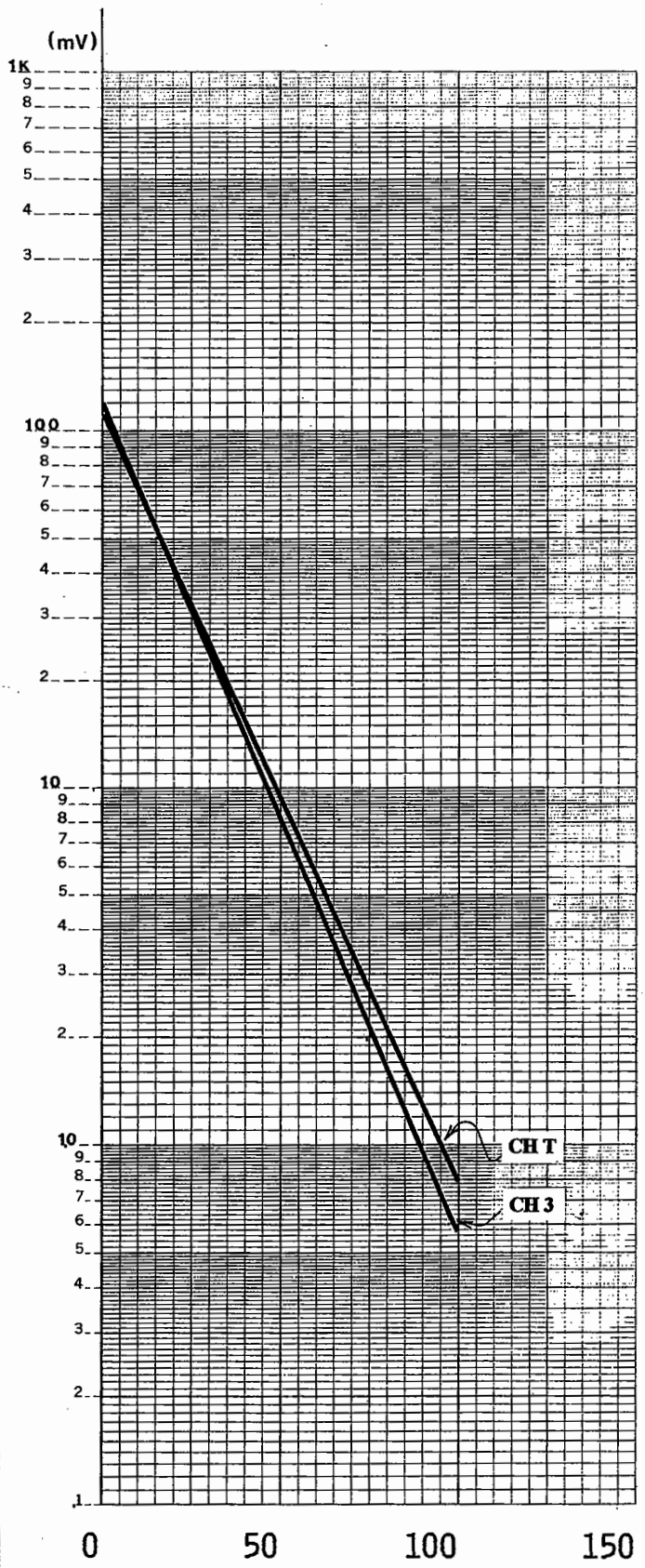
2. Sphere Response with Depth

2.1 Ferrous (Steel, Iron) Spheres

- Steel Ball 9 cm Diameter
- Steel Ball 11.3 cm Diameter
- Steel Ball 12.5 cm Diameter


STEEL BALL 9 CM DIAMETER
STEEL BALL 11.3 CM DIAMETER
(mV)
1K
100
10
1
CH T
CH 3
0
50
100
150
DEPTH BELOW SURFACE TO BALL TOP (CM)

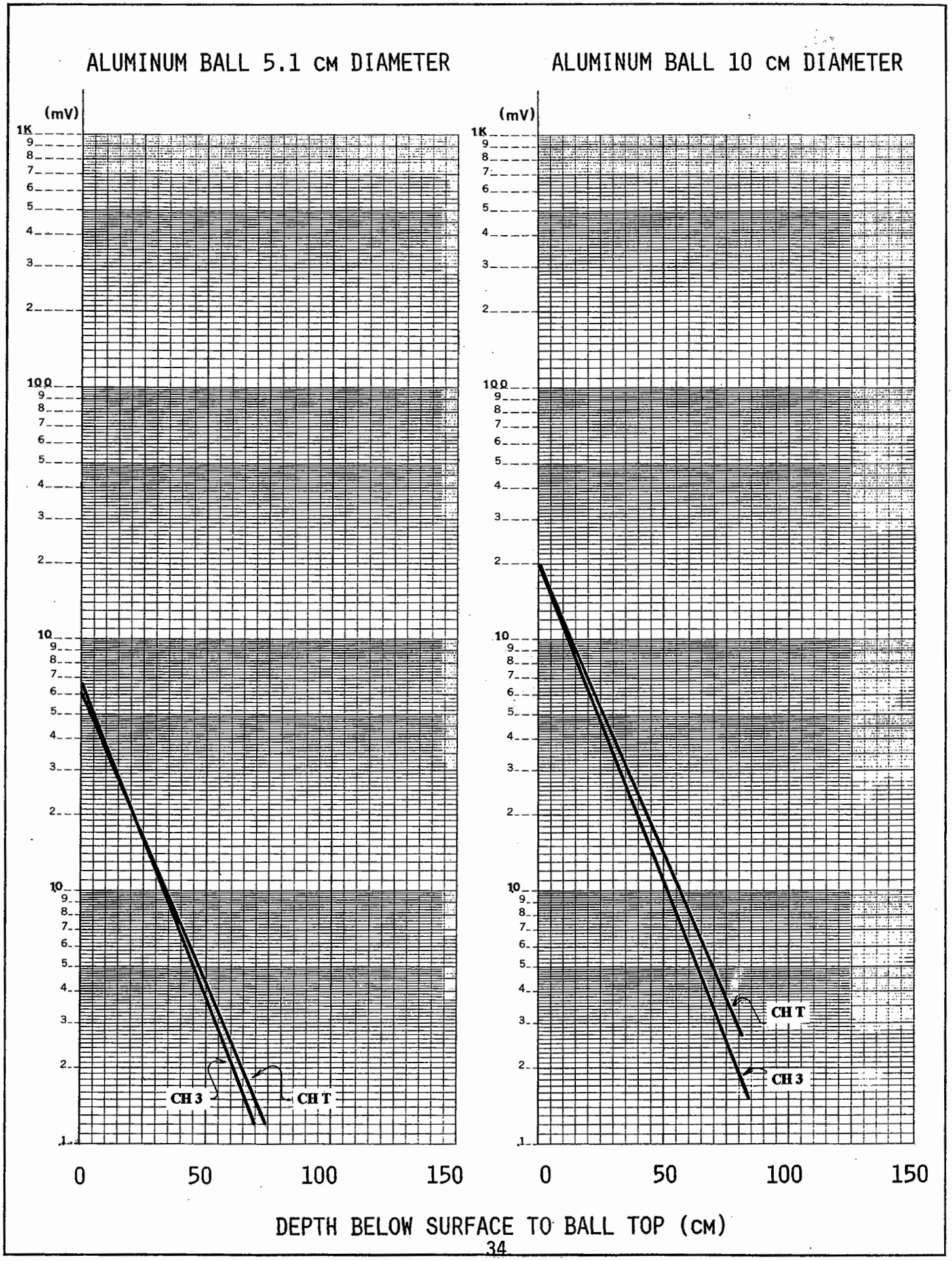
STEEL BALL 12.5 CM DIAMETER



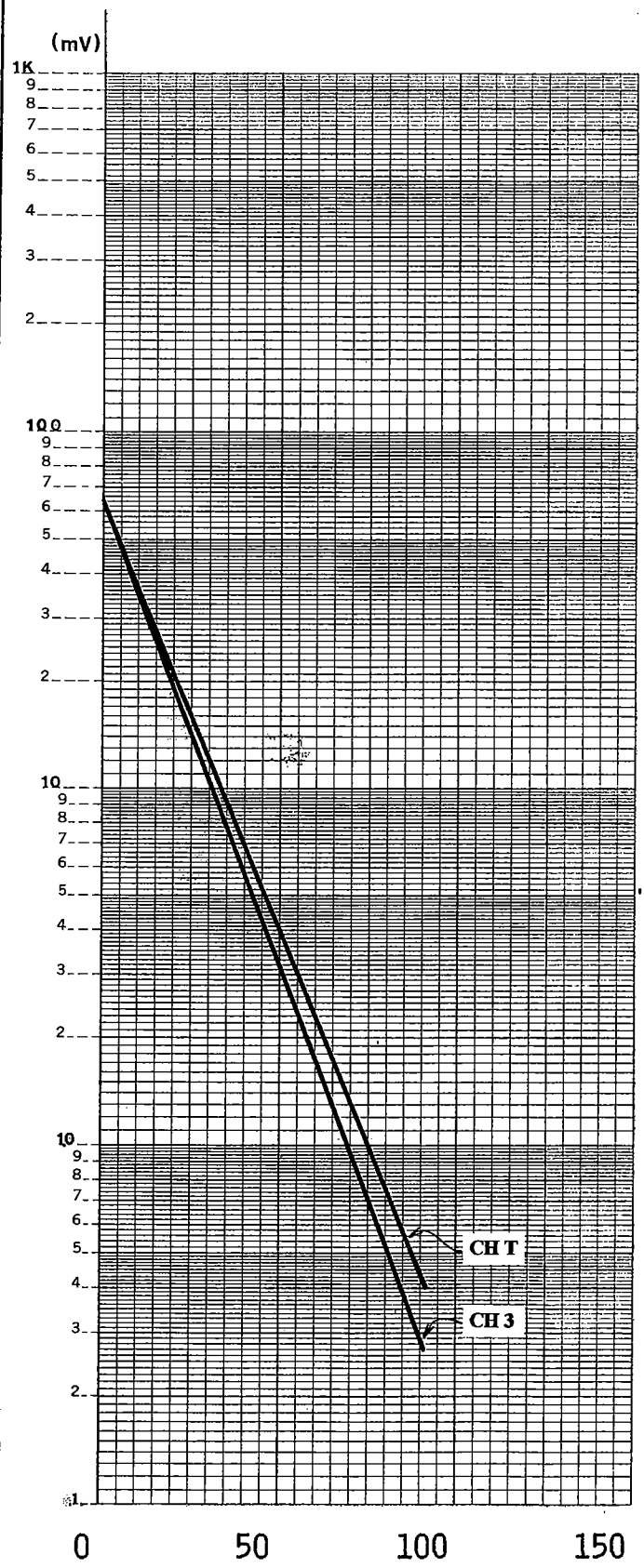
DEPTH BELOW SURFACE TO BALL TOP (CM)

2.2 Nonferrous Metallic (Aluminum, Copper) Spheres

- Aluminum Ball 5.1 cm Diameter
- Aluminum Ball 10 cm Diameter
- Aluminum Ball 20 cm Diameter

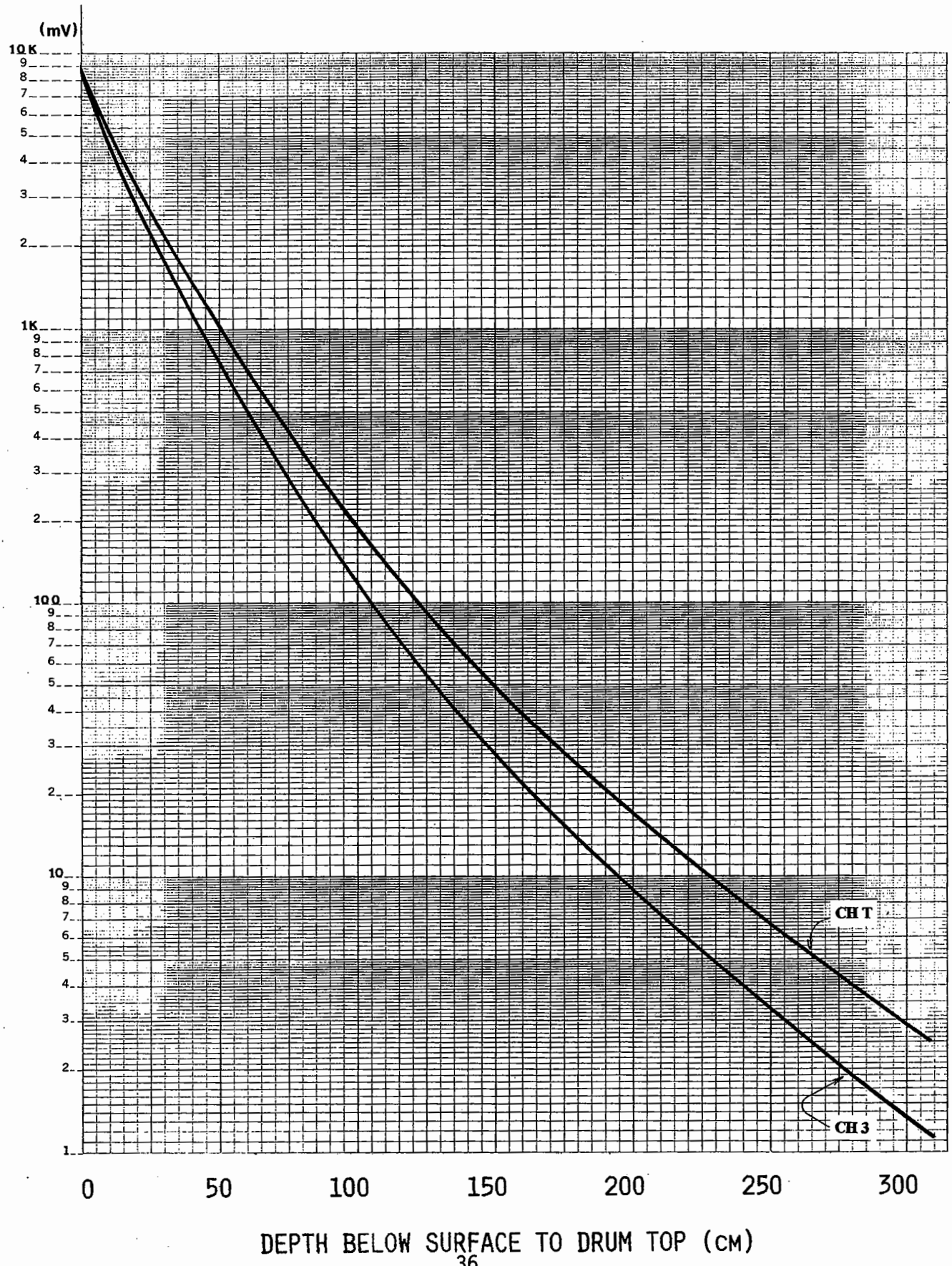

ALUMINUM BALL 5.1 CM DIAMETER
ALUMINUM BALL 10 CM DIAMETER
(mV)
1K
100
10
1
CH 3
CH T
0
50
100
150
DEPTH BELOW SURFACE TO BALL TOP (CM)

ALUMINUM BALL 20 CM DIAMETER



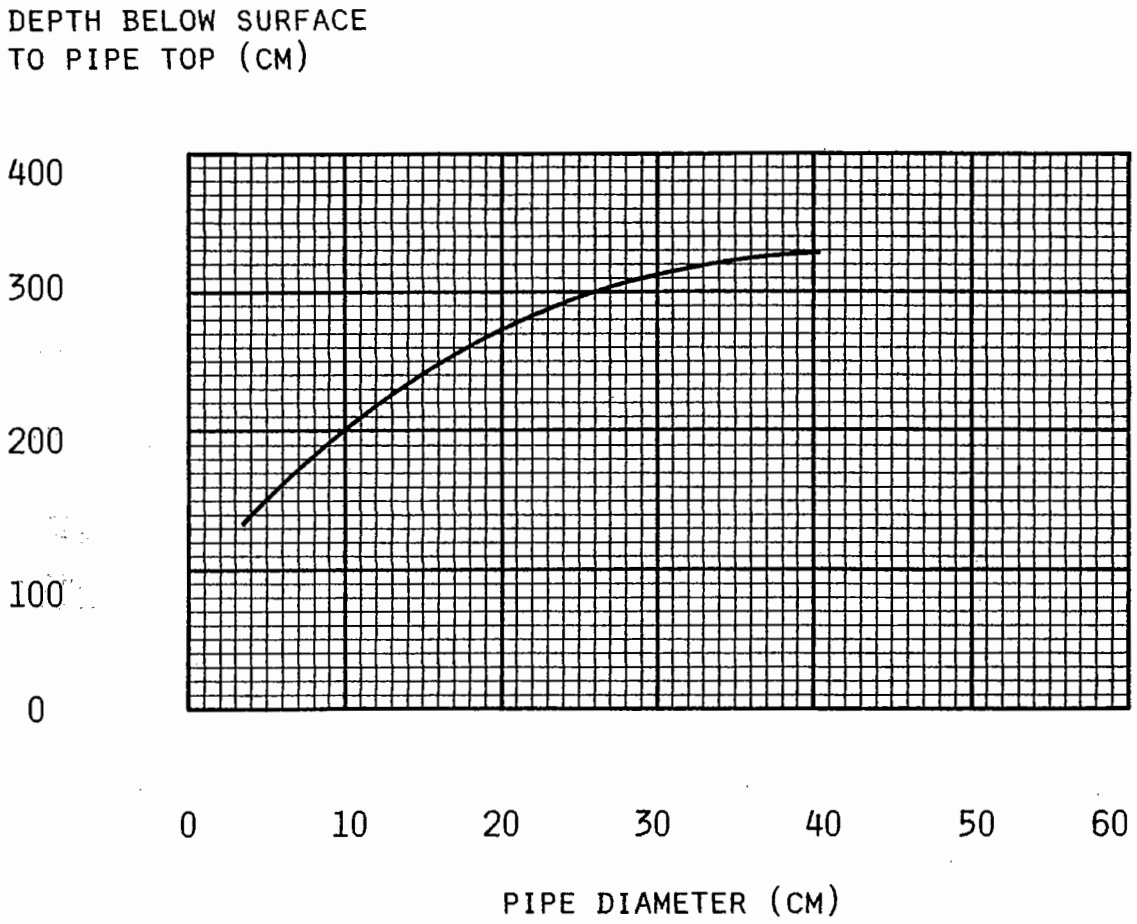
DEPTH BELOW SURFACE TO BALL TOP (CM)

3. 55 GALLON STEEL DRUM RESPONSE WITH DEPTH

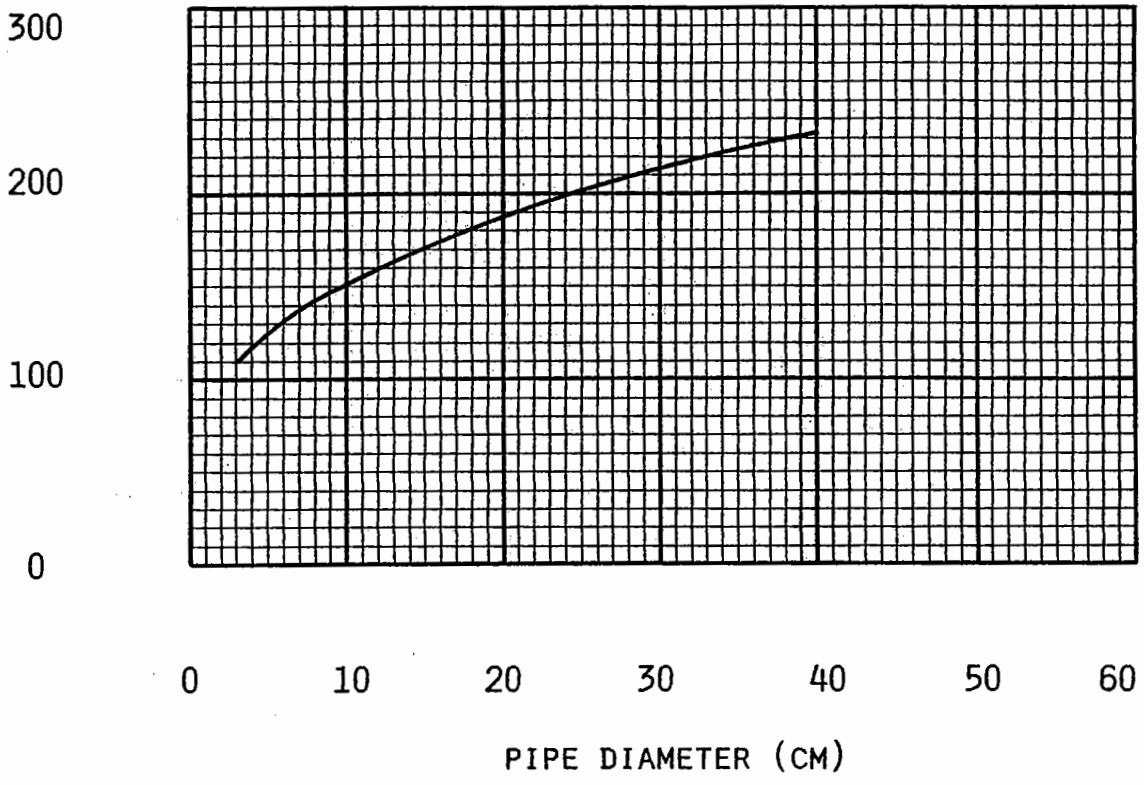


4. DETECTABILITY VS TARGET DIAMETER

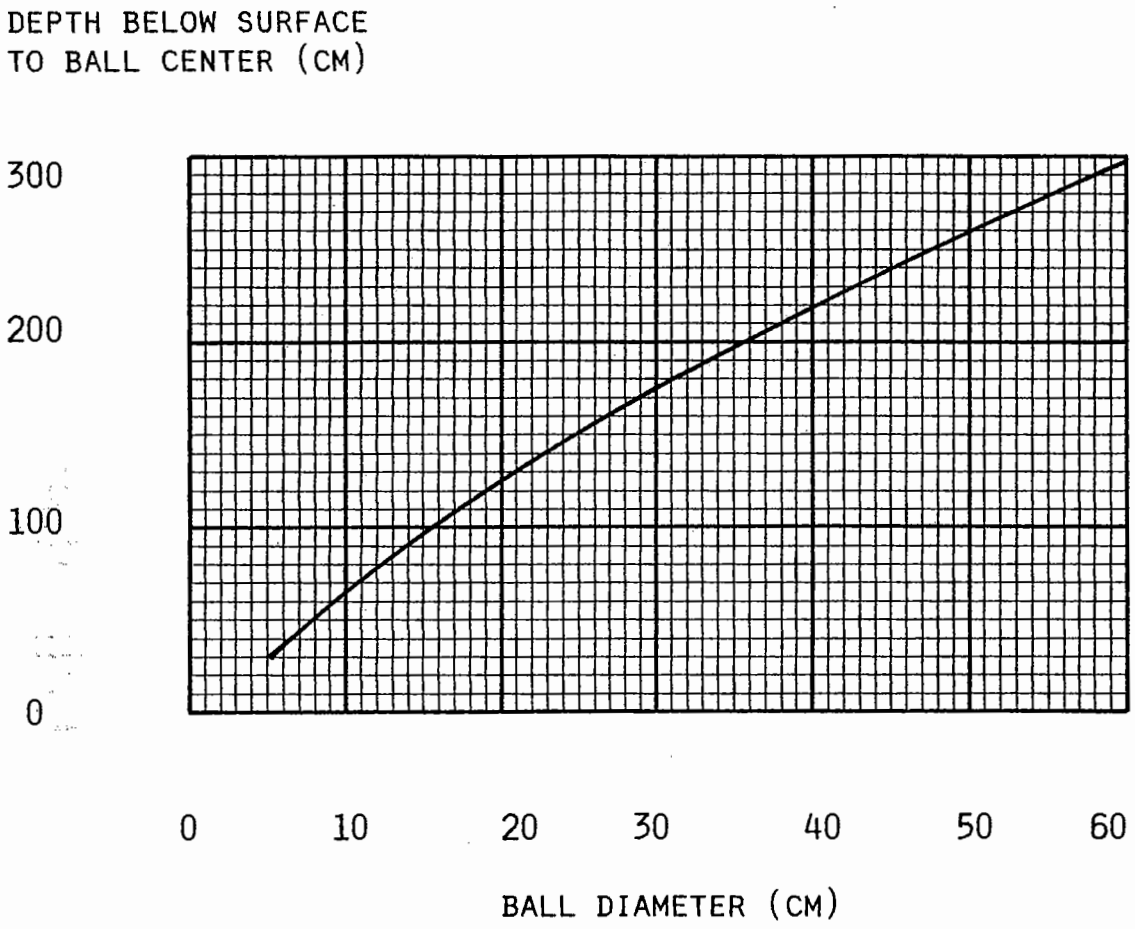
4.1 STEEL PIPE



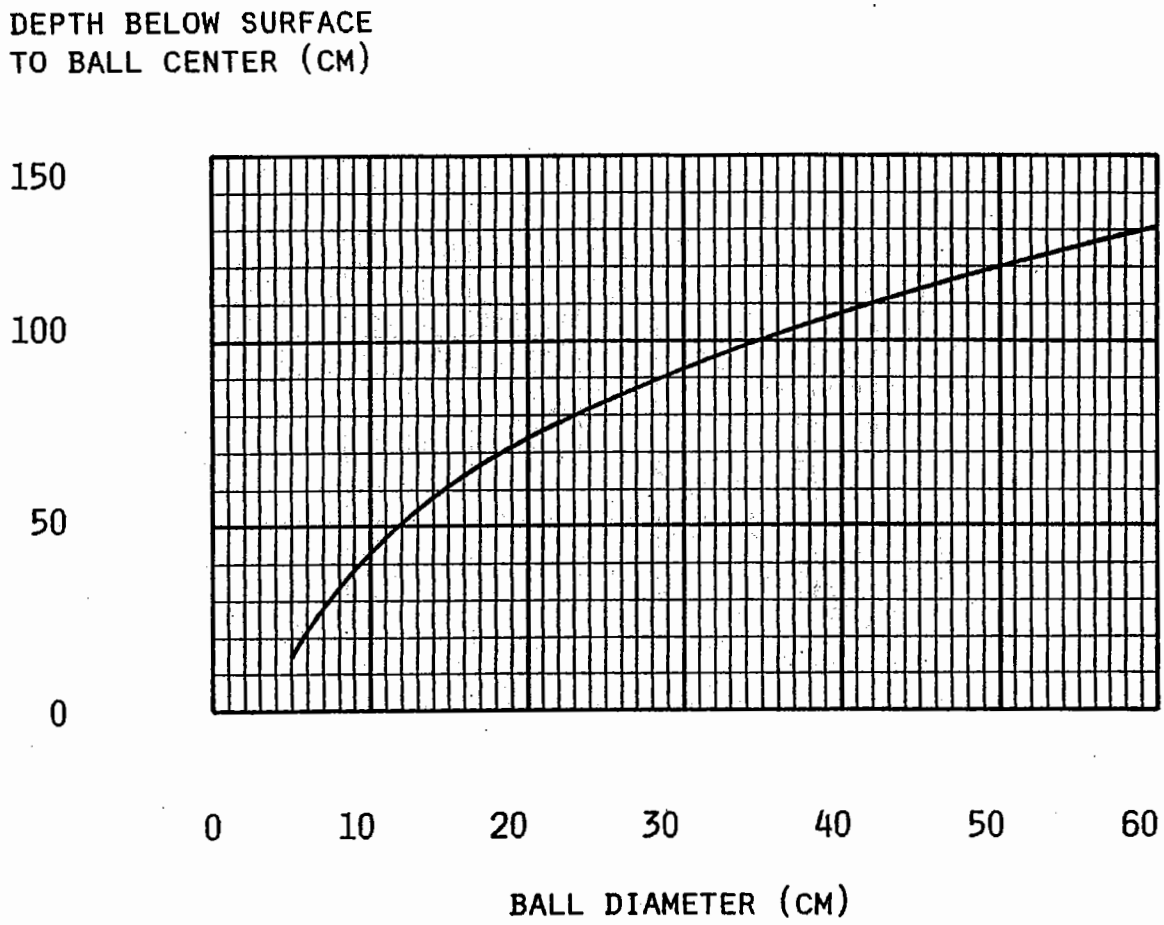
4.2 ALUMINUM PIPE



4.3 STEEL BALL



4.4 ALUMINUM BALL



G. OPERATIONAL PROCEDURES AND QUALITY CONTROL RECOMMENDATIONS

Operational Procedures and Quality Control Recommendations

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TABLE OF EQUATIONS

The EM61-MK2 consists of a coincident transmitter (Tx) and receiver (Rx) coil and a second receiver coil located 30 centimeters above the Tx/Rx coil. The Tx coil is energized by a pulse of current and the Rx coils measure the target response decay at fixed moments in time.

Figure B.1 shows schematically the EM61-MK2 coil configuration, transmitter current and induced and received signals.

The current in the transmitter coil is a series of pulses as indicated in Figure B.1a. When the transmitter current is turned off an electromagnetic force (EMF) is induced in the conductive target (Figure B.1b) with a characteristic decay which is a function to conductivity, magnetic susceptibility, size and shape of the target. The decaying current generates proportional secondary magnetic field (Figure B.1c) which time rate of change is measured by the main receiver coil (Rx 1).

The function of the second receiver coil (Rx2) is twofold: First having suitably adjusted gain in respect to the main receiver coil (Rx1), one can subtract the output signal of Rx2 from Rx1 to substantially reduce the response from near-surface targets (i.e. scrap metal) compared with deeper targets. Secondly, the relative signal output from the two receiver coils is compared to determine the depth to small targets (i.e. targets whose dimensions are small compared with the size of the coils)

The EM61-MK2 can provide output from four time gates geometrically spaced in time after the termination of the transmitter pulse. This feature allows discrimination between different types of targets based on the time-decay rate of the response. This discrimination technique works well for simple shaped targets with all three dimensions (x, y and z) being approximately equal, it has also shown to be useful, however, at some military test ranges. For additional description of the EM61-MK2 and how it can be used for discrimination please refer to Geonics Limited Technical Note TN-33[1].

[1] Technical Note TN-33, Miro Bosnar, Geonics Limited, March 2001.

A Introduction

This document is intended to provide an example of quality control procedures for the use of the Geonics EM61-MK2 and EM61 instruments. Its primary goal is to introduce procedures for surveying that will maximize data quality and promote documentation of data collection and processing procedures used by consultants. Geonics Limited would like to acknowledge for their considerable input into this document, Naeva Geophysics Inc., Geosoft Inc. and the U.S. Army Engineering and Support Center. Additional input has been provided by Peeter Pehme and Dr. John Greenhouse of Hyd-Eng Geophysics (Dillon Consulting).

B Theory

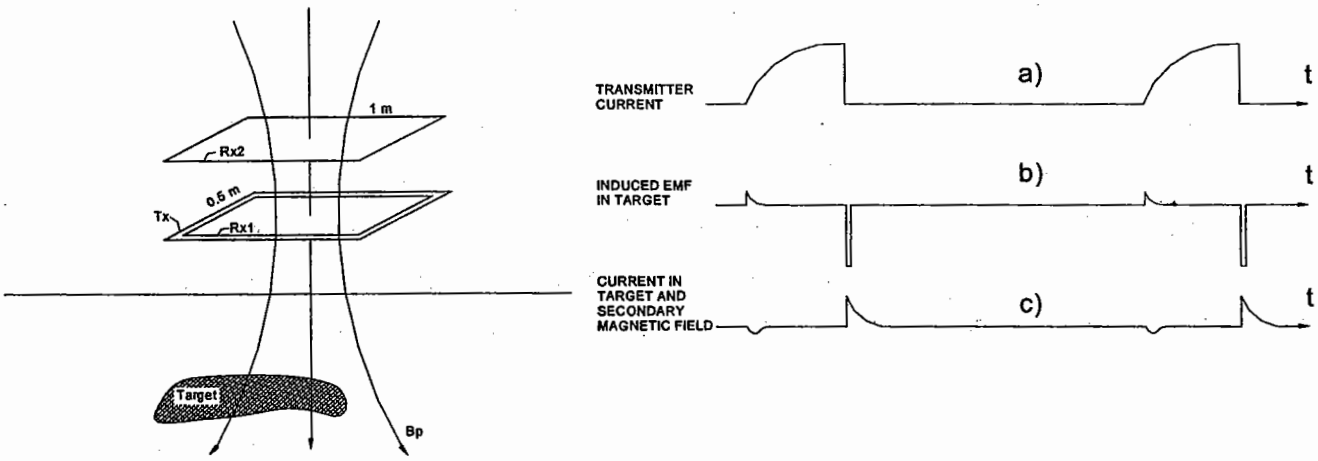

Figure B.1 Time Domain Theory

The EM61-MK2 is a time domain metal detector manufactured by Geonics Limited of Mississauga, Ontario. The instrument is used for the detection of ferrous and non-ferrous metallic objects primarily in the environmental/engineering and unexploded ordnance (UXO) applications.

The following is a short description of the time domain electromagnetic induction principles as it applies to metal detection.

C Planning

The following list for planning geophysical surveys is limited to a brief description of major elements for brevity. These elements are standard for planning any geophysical investigation and have been referred to in various documents. Many of these elements are considered to be standard by the Environmental and Engineering Geophysical Society (EEGS).

C.1 Research Site History.

a. Review all previous investigation reports. The previous usage of the site and the likely composition and depth of targets should be defined in this stage of planning.

b. If possible, conduct interviews with personnel formerly assigned at site. One goal of the interviews may be to obtain local information and anecdotes on the suspected target areas.

C.2 Research Site Geology.

a. Review surficial geology: Obtain geologic maps and literature for the site.

C.3 Preparation of Geophysical Investigation Plan.

a. Determine survey type: Random, Fixed Pattern Transects, or Detailed. Survey type is dependent on the objectives of the investigation, whether the goal is to conduct Geophysical Sampling, Geophysical Mapping, or a more detailed Geophysical Investigation.

b. Determine methods and procedures proposed for the investigation: Methods and procedures are determined by consideration of all factors described above, as well as type and expected depth of targets. Topography, vegetation, and the presence of cultural features must also be considered in the selection of instruments: standard, hand held, and high power.

c. Determine required data density, based on type of investigation: Size and depth of expected targets, and method used for detection will dictate minimum requirements for line and station spacing.

d. Define method of navigation, means of location and mapping: Describe procedures and equipment to be used in data collection to ensure accurate location of data points. Means of location and mapping points, whether by GPS, ultrasonic or through conventional surveying of grid corners should be defined.

e. List survey equipment and services: Prepare list of items needed to perform survey, and services required. List should include sources of supplies and rental sources of equipment that may provide backup instruments in the event of instrument malfunction.

f. Describe Data Storage, Transfer and Archiving.

g. Describe Quality Control procedures to be performed: steps to ensure proper instrument function, accurate mapping and location of anomalies, and repeatability.

h. Describe Procedures for Reacquisition: methods of reacquisition of anomalies.

i. Define Work Schedule, project completion, schedule of deliverables to client.

D Amplitude Response and Depth of Detection

D.1 Introduction.

Test measurements have been made at numerous sites on inert ordnance items at various depths and orientations. It has been shown that the approximately dipolar amplitude response of small target items is inversely proportional to the distance of separation between the sensor and the anomaly source. Theory as well as testing has also revealed that ferrous targets vertical ferrous targets generally have a greater EM amplitude response than horizontal and the opposite is true for nonferrous objects. Table 4.1 depicts a number of EM61 amplitude response measurements over horizontal ordnance items and calibration spheres at various depths.

a. The typical noise level for a well maintained and calibrated EM61-MK2 is about 1 to 1.5 mV (for the EM61 or channel #3 of the EM61-MK2). Therefore, the depth at which each ordnance type response reaches signal that is two time of this noise level is defined as the detection depth for that object. At various locations across a remediation site, the

local terrain noise will reduce the actual detection depths. It is inappropriate to speak of a 'typical detection depth' for a particular instrument without considering terrain noise.

The standard EM61-MK2 cannot detect single objects at depths much greater than 3-4 meters. For objects greater than 3 meters, the high power and/or larger transmitter loops are generally recommended.

EM61-MK2 / EM61-MK2-HP (High Power)

UXO Detection* Depths

Target Type	Detection Depth Below Surface (cm)			
	Vertical Target Orientation		*Horizontal Target Orientation*	
	MK2	MK2-HP	MK2	MK2-HP
20 mm Projectile	58	100	8	15
20 mm Cartridge	68	120	38	72
40 mm Dummy Round	68	120	66	118
60 mm Mortar	88	145	64	110
81 mm Dummy Round	108	175	95	150
105 mm Projectile	152	230	114	177
155 mm Projectile	200	300	140	210
500 lb. Bomb	500	700	320	445

** detection at 2mv response in 1 mv noise environment*

Table D.1 Detection Depths

b. The Ordnance Detection and Discrimination Study (ODDS) conducted by Parsons Engineering Science for the Corps of Engineers at the former Fort Ord in California, in July 2000, generated excellent examples of static test data using vertical gradient magnetometer and EM (time domain and frequency domain). Figure 4.2 was compiled using ODDS data, illustrating their findings on maximum depths of detection for 187 different ordnance items, ranging in size from a 14.5 mm trainer M181 projectile, to a 155 mm projectile. It is important to note that all of these measurements were recorded using a special platform, raised above the ground surface with low ambient noise. The following comments can be made:

(1) Maximum depth for each item was the calculated maximum depth of detection for soils at Fort Ord. For the EM61, best and worst orientations were generally with the long axis of the item vertical, and horizontal, respectively.

(2) Readings as low as 1.49 mV were recorded as detectable for the EM61, and 1.31 mV for the EM61-HH. While these numbers may be useful in calculating detection depths in an ideal environment, in a real survey noise levels from a variety of sources will probably necessitate a higher threshold. Additionally, the better signal to noise ratio and earlier time gates of the EM61-MK2 will improve the detection level of both smaller and deeper targets.

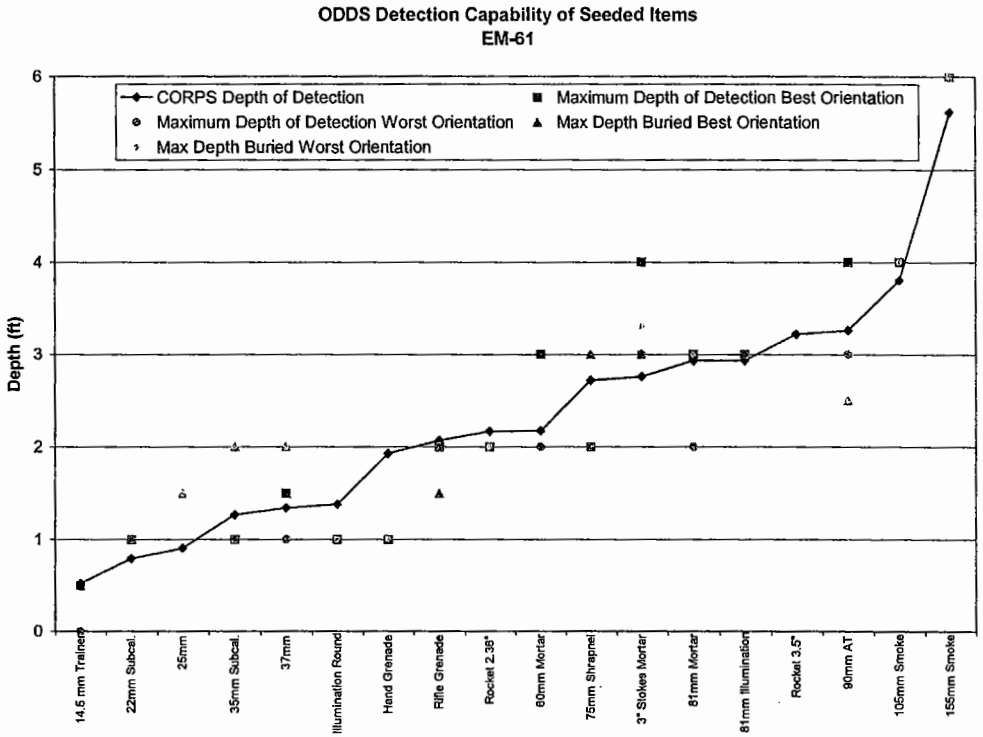

Figure D.1 Fort Ord Detection Depths –EM61

D.2 Geophysical Noise

a. The responses of targets may be detected only if they are greater than the background noise level. Geophysical noise (not sensor sensitivity) is therefore the limiting factor in determining thresholds and detection depths. The noise encountered in geophysical surveys is generally of four types:

- Instrument Noise
- Ambient (electromagnetic) Noise

- Motion or Dynamic Noise (mechanical vibration, etc.)

- Terrain Noise (site-specific, repeatable response of rocks, soils, and metal clutter)

b. Instrument noise is internal and intrinsic to the instrument. It is generally, by design, of much lower amplitude than other sources of background noise. Ambient noise is induced in the sensors by outside electromagnetic fields in its vicinity. It can be caused by nearby powerlines, motors, radio transmitters, generators, radar, and other electrical or electromagnetic devices. GPS electronics and radios are common sources of ambient noise.

c. Motion noise is caused by mechanical vibration of the instrument and metal on the operator or instrument (wheels, etc.). It can occur anytime the instrument is moving. Varying the EM61-MK2's coil(s) orientation while surveying may generate a high frequency (depending on rate of change) response which can make interpretation of smaller targets difficult. This "noise" likely results from varying the instruments sensors in a manner that the coupling with the earth's magnetic field is changed.

d. Terrain noise is cause by real and repeatable instrument response to highly magnetic rocks and soils, and metal clutter. The term terrain refers to the sources of response that are actually present in or on the ground. It is usually the largest noise component and often the limiting factor in geophysical detection and interpretation.

D.3 Filtering Noise.

a. One frequently hears references to 'filtering the noise'. Short wavelength and long wavelength noise can be suppressed by filtering. Unfortunately, terrain noise often contains the similar wavelengths as target responses and therefore cannot be easily removed by spatial filtering.

b. Static (bench) tests measure the sum of instrument and ambient noise (and also instrument drift). Dynamic tests along an actual survey line are necessary in order to measure motional and terrain noise. A repeated dynamic test survey line also measures positional variation.

E Equipment Functionality and QC Tests

The recommended equipment tests and frequency of testing is summarized in Table 5.1.

E.1 Out of Box Equipment Tests

Non-functioning equipment arriving at the site will cause delays in surveying. Worse yet, improperly functioning equipment may result in unreliable data, increasing false alarms or missing targets. For these reasons out of box equipment tests are recommended to ensure instruments are operating correctly:

a. Inventory and inspect all components. Geonics provides a packing list showing all included components. Check that each item is present, and inspect cables, connectors, harnesses, etc. for signs of wear or damage. Spare cables are essential as the cables are often the most vulnerable part of a system.

b. Assemble the instrument and power up.

c. With the instrument held in a static position, and collecting data, move cables to test for shorts and broken wires or pins. Shake cable starting on one end and proceeding to the other. An assistant is helpful to observe any changes in instrument response. If shorts are found, mark cable, set aside and replace.

d. Conduct Static Test, and Instrument Response Test:

(1) Establish an area for these tests that offers convenient access, is free of metal (surface and sub-surface), and is sufficiently far from roads and power lines, transmitters, etc. to avoid these sources of noise. This same point should be used throughout the duration of the project for the daily static and response tests and for instrument nulling.

(2) Static Test: The purpose of performing a static test is to determine whether a particular geophysical instrument is collecting stable readings. Improper instrument function, the presence of local sources of ambient noise (such as EM transmissions from high-voltage electric lines), and instability in the earth's magnetic field (as during a magnetic storm) are all potential causes of inconsistent, non-repeatable readings.

The operator must review the readings to confirm their stability prior to continuing with the geophysical survey.

(a) When the instrument has been powered up sufficiently long to warm the electronics (2 to 5 minutes), place the instrument at its normal operating height and orientation so that it will remain stationary and begin data collection. (An alternative to waiting for the instrument to warm up is to begin data collection when the instrument is turned on, thus documenting the time required for readings to stabilize.) Collect readings for a minimum of three minutes after instrument warm-up. Data collected during static tests should be retained for documentation purposes. This site should also be used to "NULL" and "calibrate" the EM61-MK2; refer to the operating manual for a detailed explanation of this procedure.

(b) The effects of ambient noise may vary across a project site. Therefore, it may be necessary to perform several static tests across the survey area.

(3) The Instrument Response Test using QC coil as per description in section A2 of this manual quantifies the response of the instrument to a standard test item. A steel trailer ball can also be used as a test item that is easily acquired and transported. A standard 2" diameter trailer ball with integrated shaft could be used as the test item. Leaving the instrument in the same position as used in the Static Test, activate the QC coil or place the test item below the sensor, and then collect data for a minimum three minute period. The test will document the amplitude of response to the test item and instrument drift.

E.2 Initial Geophysical Instrument Checks

These tests are performed the first day of a geophysical investigation.

a. Six-Line Test: This test can be used for all geophysical instruments, and is illustrated in Figure 5.1.

(1) Use an area that has little background noise and no sources of anomalous responses.

(2) The test lines should be well marked to facilitate data collection over the exact same lines each time the test is performed. Background response over the test area is established in Lines 1 and 2.

(3) A standard test item, such as a steel trailer hitch ball (or any metallic object) will be used for Lines 3 through 6. Heading effects, repeatability of response amplitude, positional accuracy, and latency are evaluated in Lines 3-6.

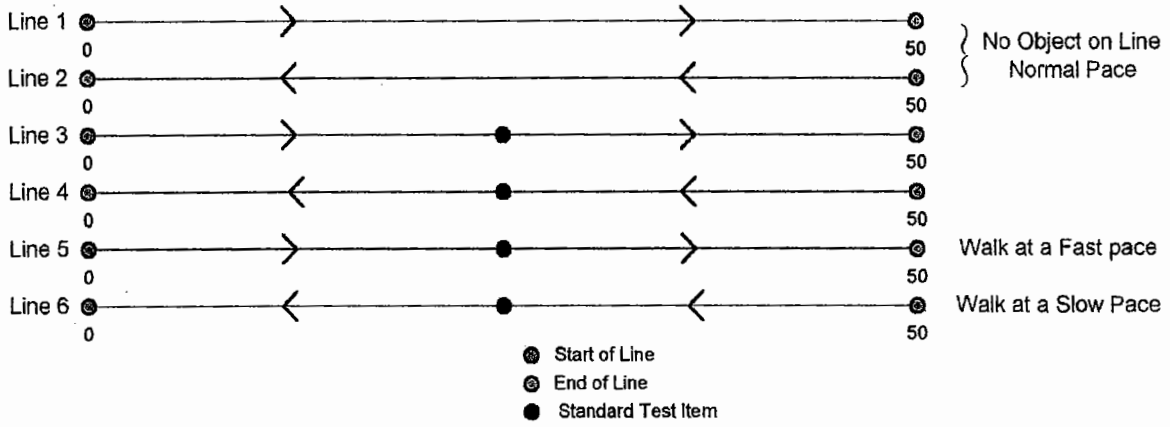

Figure E.1 Example Test Site

b. Pull-Away Test: This test demonstrates the effects of navigational equipment and/or vehicles used to tow sensors or arrays. With the instrument collecting data in a static (background) test, navigational equipment and/or vehicles, positioned as they would be in the field survey, are pulled slowly away from the sensor to gauge any differences in response. This must be performed twice; once with the navigational equipment (and/or vehicle) power off, the second with the equipment powered up. A simple DC shift may be observed when the equipment is in normal operating position, compared to values when it is distant, however this is easily removed from the data. However, a DC shift greater than 50 mVolts should not be considered insignificant and will affect the instruments sensitivity. If excessive noise (or shift) is noted, however, steps should be taken to identify the source and correct the problem.

E.3 Suggested Daily Instrument Checks.

a. Cable Shake Test: Prior to collecting data each day, the instrument cables and connectors should be tested for shorts as described in the out of box equipment tests. Faulty cables or connectors will be replaced prior to data collection.

b. Static Test (Background): This test should be performed twice daily in the same location, prior to data collection, and at the end of the day. Data should be recorded during a minimum 3-minute duration static test to demonstrate stability of readings over both the short and long term.

c. Static Test (Response): Following the static background test, a QC coil or standard test item should be used, and readings recorded for at least 3 minutes. Instrument response of equal amplitude from test to test demonstrates that the calibration of the instrument has not changed. (This test should be repeated when changing batteries.)

d. Personnel Test: The instrument operator moves around the stationary, operating instrument to scan for any effects from remaining metal on the operator.

E.4 Examination of Repeat Data.

A minimum of 5% repeat data is recommended for grid sampling. Repeat lines should be adjacent to one another. A site with a low density of anomalous responses would benefit from a higher percentage of repeat data. When viewed in profile and compared to original data, repeat data provides a means of evaluating the ability of the instrument to respond consistently, and evaluates the positional accuracy of the data. Errors in positional repeatability indicate a problem in the method of navigation.

Test	Frequency of Testing		
	Beginning of Day	Beginning and End of Day	First Day of Project Only
Personnel Test	X		
Cable Shake	X		
Static (Background)		X	
Static (Response)		X	
6 Line Test			X

Table E.1 Instrument Test Table

F Data Acquisition

F.1 Survey Design Elements.

a. Line spacing requirements for grid sampling are dependent on the specific geophysical instrument being used and the types of buried targets expected. Geophysical investigations for the more common munitions types (mortars, grenades, projectiles, etc.) that are buried randomly require standardized intervals between lines. The following line spacing has been mandated by some United States military organizations and is recommended for munition site surveys.

	Line Spacing	
Instrument	*English*	*Metric*
EM61 (meter wide footprint)	2.5 ft	0.75 m
EM61/ EM61-MK2 (half meter wide footprint)	1.5 ft	0.5 m
EM61-HH	1 ft	0.3 m

Table F.1 Line Spacing Recommendations

For other instruments, alternate line separations may be necessary.

In cases where small, shallow depth munitions with low amplitude responses are being investigated, it may be necessary to reduce line spacing to one-half the diameter of the receiving coil. Such reductions in line separations will have an adverse affect on production rates. When the objective is to find large, deeply penetrating items or burials (caches, pits, and trenches) line spacing can be increased to suit the situation. Adequate data density is determined by the same factors as adequate line spacing. However, increasing data density along survey lines usually does not significantly increase survey time or cost. Increased data density improves the likelihood of a reading being taken directly over the peak of an anomaly. The following are minimum data densities for the EM61, EM61-MK2 and the EM61-HH. When operating in automatic sampling mode, the consultant must determine the appropriate sampling rate and operator speed in order to achieve these intervals. As with line spacing, if the objective is to find large, deeply penetrating buried munitions items or burial features, data density may be decreased to suit the situation.

	Data Density	
Instrument	*English*	*Metric*
EM61 (meter wide footprint)	0.66 ft	0.20 m
EM61/EM61-MK2 (half meter wide footprint)	0.66 ft	0.20 m
EM61-HH	0.33 ft	0.10 m

Table F.2 Station Spacing Recommendations

b. Meandering Path and Transects: These types of surveys are alternatives to grid sampling that may offer advantages in some investigations. Line spacing for a Meandering Path survey is influenced by vegetation density, as denser areas are avoided. Transects use a fixed spacing between lines. When used in this manner transects may be considered as very narrow grids. Data density in both types should meet the requirements listed above. Unlike standard grid sampling, all of the data in Meandering Path and Transect surveys is subject to edge effects. Passing close to or over the edge of an ordnance item reduces the amplitude of the response compared with traveling directly over it. As a result, different thresholds must be considered for selection of anomalies in these types of surveys. Another important difference versus grid sampling is that the collection of repeat data may not be possible.

c. File Naming Conventions: A standardized format for file names should be used throughout the duration of a project, and should also be documented. A logical format, incorporating information such as Date, Area, Sector, and Grid # is suggested. For standardized tests that are recommended to be repeated twice daily, such as Static Background, the file name should include the date, the type of test, and an indication of whether it is AM or PM. Note: the Polycorder provided with the standard EM61 limits the number of characters for a file name to 7. The field PC provided with the EM61-MK2 defaults to a date: time file name that can be edited to include the suggested parameters.

F.2 Operating Procedures for EM61 and EM61-MK2

a. All EM61s have been designed to keep the operator far enough away from the coils so that small amounts of personal metal will not influence the data. Regardless, pockets should be emptied of coins, knives, etc., and wristwatches removed. Small amounts of metal such as wire-rimmed glasses, earrings, etc. are not detectable by the instrument,

and are distant enough in normal use that they cannot cause problems. Steel-toed boots can have a profound impact on data. Steel shanks commonly found in boots are less problematic than steel toes, but should be avoided as the feet may closely approach the coils during data collection. The high sensitivity of the EM61 Hand-Held coils increases the likelihood that metal components in footwear may compromise data quality. Carefully inspect the operator for metal. Removing metal from the operator is most critical when operating the EM61 in harness mode because the operator is inside the coils.

b. The operating manuals of most geophysical instruments do not include a discussion of a warm-up period prior to collecting data. However, all geophysical instruments undergo a short period of reading drift as the system electronics warm-up. Instruments should be allowed to warm-up a minimum of 5-15 minutes every time they are turned on or the battery is changed. Low ambient temperatures will demand a longer warm-up period. The geophysical team will carefully examine the readings to ensure that they have stabilized.

(1) Figure 6.1 illustrates drift typically seen in the warm-up period for an EM61. Performing a static test will quantify this warm-up reading drift and at the same time satisfy the need to document ambient noise at the site. The static test shown in Figure 6.1 exhibits very low background noise. In this example, a standard EM61 was operated in Auto Mode (extra fast), collecting approximately 8 readings / second. The ambient temperature was approximately 70 degrees F. The instrument electronics warmed up and produced stable readings in less than three minutes.

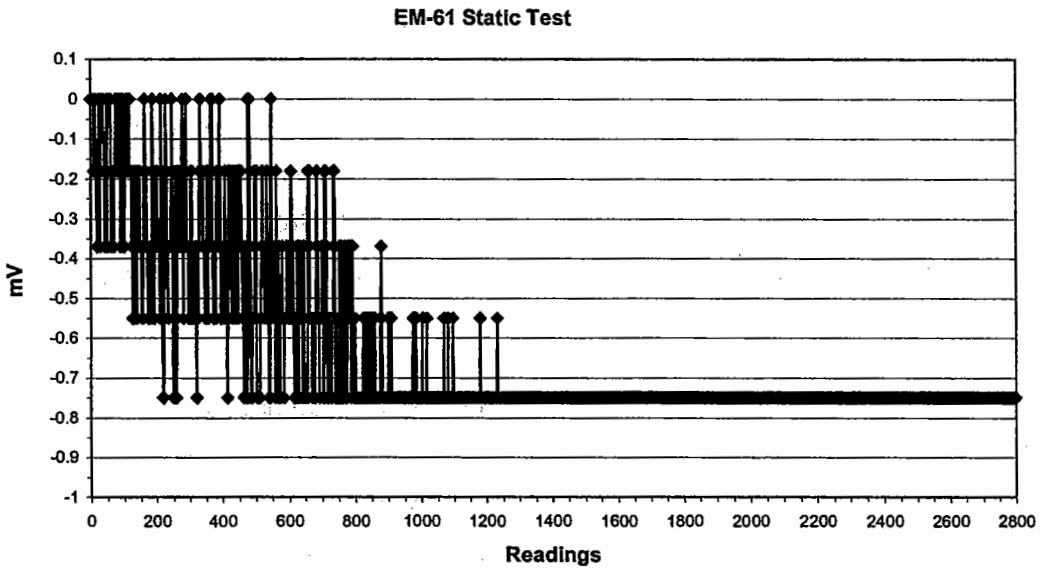

Figure F.1 Instrument Warm Up

c. Check battery levels and record in field notebook or grid survey form before and after data collection. EM61 batteries should be replaced when the voltage falls to 10.5 volts.

d. The rates of data acquisition for EM61's are limited by the processing speed of the data logging system. A minimum amount of time is required for the system to process and record each reading. If a second reading is triggered before the first is recorded, the data logger (polycorder) will 'beep' and the first reading will be dropped. This results in an incomplete data set.

(1) Using the standard EM61 or EM61 Hand-Held in Wheel or Hip Chain mode, the options of Full, Partial, or No Display are available at the start of each file. The Full option will display data after conversion to millivolts and allows the collection of 4 readings per second. The Partial setting displays data as unconverted raw voltage, allowing a collection rate of 8 readings per second. No Display shows only the present station coordinates, resulting in available collection rates of 8 readings per second.

(2) When starting a new file, a standard EM61or EM61 Hand-Held in Auto Mode offers the options of User Defined / Fast /Extra Fast data collection rates. The User Defined option is capable of recording up to 4 readings/second. The Fast option records 5 readings/second without GPS and 4 readings/second with a GPS time

stamp. The Extra Fast mode collects 8 readings/second without GPS and 7 readings/second with a GPS time stamp.

(3) The EM61 MK2 uses a more sophisticated Juniper Systems Pro 4000 or Allegro field PC. The maximum data acquisition rate increases to 19 records/second, with each record consisting of four sampled time gates per station and, optionally, position data.

e. Older EM61 wheels contain a limited amount of metal that is distributed unevenly within the rim of the wheel. As a result, these wheels can cause periodic anomalous responses of several millivolts or more as measured by the bottom coil. With a low enough target selection threshold, the wheel responses may be incorrectly interpreted as being representative of subsurface metal.

(1) Alternatives to using the older hard rubber EM61wheels include substituting either EM61 Handheld wheels or the most recent standard EM61-MK2 wheels which have solid foam tires. Both types of wheels are free of any metal components and can be easily mounted on the EM61 axles.

(2) In addition to metal components in the wheels themselves, wheel noise can be introduced by nails or metal fragments embedded in the tires. This may also cause periodic anomalous responses as the object rotates past the coils. EM61-MK2 wheels will be carefully inspected throughout the data collection process in order to minimize this problem.

(3) Should wheel noise be suspected during the project, the following test can be performed. Invert the EM61-MK2 and conduct a static test for one minute followed by collecting one minute of data while slowly spinning each wheel. Any additional noise present in the portion of the file collected while a wheel was spinning is likely due to the presence of metal somewhere in that wheel.

f. Loose, dangling cables could potentially cause anomalous responses in EM61-MK2 data. The cable connecting the coils to the backpack should be temporarily attached to the handle (with tape, Velcro straps, etc.) in order to eliminate the cable as a source of geophysical noise.

g. At the start of every project, the geophysical consultant will establish a nulling and calibration station where the top and bottom coils can be leveled. The nulling station must be established in an area free of metal, with no interference from sources of ambient noise. Mark the center of the nulling station with a semi-permanent, non-metallic marker, to ensure consistent placement of the instrument each day. The station should be placed in the same spot as the static test station and will also be occupied at the beginning and end of each work day. Early model EM61s have no means for nulling or calibration, therefore data must be leveled during post-processing.

h. If GPS is to be used and logged to a separate recorder from that of the EM data, synchronization of the internal clocks is critical for accurate location of data. Once the clocks are synchronized, data collection may begin. It is recommend that you open a test/calibration data file in both data loggers and attempt to begin taking actual measurements at exactly the same time. It is recommended that this be completed at the start and end of each day as the clock in some DL600s is known to drift. (<1sec/24hours). This will get you to sub-second accuracy depending on how fast your fingers are. Additionally a known calibration "site" where a known EM target exists (such as a 6" spike driven into the ground) should be established. Locate the station accurately with the DPGS, and then collect data across the target a number of times in the same fashion, as you would be conducting your survey. It then becomes a simple spread sheet task to match the peak instrument response and time with the DPGS known target location. This information is then used in the DAT61W program.

i. During data acquisition, the operator will pay close attention to sounds emitted by EM61/MK2 backpack and the data logger to evaluate instrument function and data quality. Continuous, audible response may be indicative of metal stuck to the instrument or the effect of a low battery. No audible response over visible metal objects may indicate another sort of instrument malfunction.

j. The operator should note the presence of all sources of potential EM interference (objects that will affect the instruments response). These comments should be noted digitally on the instruments datalogger. The EM61/EM61-MK2 data acquisition systems allow for comments to be embedded in the data; thereby the correct position of the

surface metal (or other source of interference) can be noted on the interpretation diagrams.

G Navigation

G.1 Introduction.

Prior to the advent of GPS and other electronic navigation systems, geophysical data was collected and positioned using local coordinate systems. In recent years, GPS in particular has become an increasingly popular tool for geophysical surveys at buried munitions sites. The latest systems are capable of providing, under the right circumstances, positional accuracy measured in centimeters. Despite this, the use of local grids and conventional methods is still preferred in many circumstances, as it provides a high degree of accuracy at low cost, regardless of obstructions such as overhead tree canopy.

G.2 Conventional Navigation

These methods involve placing temporary markers on the ground surface in order to establish data collection lines. In a typical grid layout, the markers allow the operator to traverse the grid using straight, parallel lines and ensure that the entire area has been covered.

a. Grid set-up begins with the establishment of line separation and length in the required units (meters or feet). If squared grid corner stakes are already in place, tape measures can be pulled between them on all sides. Tape measures and/or surveying equipment (transit, compass, etc.) can be used to establish right angles if no grid stakes are present.

b. Fiducial marks (known locations entered into the data during collection) will be placed on the ground using temporary markers. Temporary markers commonly used for fiducial locations include measuring tapes, marking paint and ropes. The distance between fiducial marks is dictated by site conditions; less visibility due to rolling terrain or dense vegetation will require closer spacing.

c. Using conventional navigation methods, it is essential that straight-line profiling be maintained. The operator must have easily visible monuments along which to walk. Fiducial ropes with paint marks at every line location will accomplish this. Another commonly used method is to place traffic cones at the start, end and at intervals along

each line. The use of cones requires the operator or other team members to move them as data collection proceeds.

G.3 Global Positioning System (GPS)

This method of navigation has increased in popularity in recent years, as the accuracy of the positions has increased. Software for most Geonics systems now includes a means of integrating GPS positions with geophysical data.

a. Standards for Equipment: GPS equipment varies drastically in price and quality, therefore the consultant should determine a minimum standard for equipment to be used in Digital Geophysical Mapping (DGM) surveys.

(1) Small hand-held units manufactured for recreational use are not usually acceptable for DGM work. These units typically cost $150 to $400, and while helpful for finding general locations, are not capable of the level of precision necessary for geophysical surveying. These types of GPS units can achieve accuracies of approximately 30 meters. WAAS enabled systems claim accuracies of 3 metres – but with generally no mention of acquisition time required to achieve these accuracies.

(2) The use of Differential GPS (DGPS) allows for the correction of errors in positioning from several sources, which include clock errors, atmospheric effects, and signal reflections. Accuracies within a meter or two are possible using DGPS, given favorable conditions. Differential GPS making use of the Carrier Phase permits accuracies within centimeters. Correction of bias factors may be accomplished in real time, using a Real Time Kinematic (RTK) GPS system, or through Post Processing. RTK systems utilize a base station, set up on a known point, which then transmits corrections to a roving GPS unit via radio. Post Processing techniques also rely on base stations, which can be set up on site, or can be a remote station. Base station data is used to apply a correction vector to the rover data. The level of accuracy required for a specific project depends on the goals.

b. Minimum Standards for Data Quality: The number and location of satellites visible to the antenna, and the presence of obstructions influence the level of accuracy for a GPS reading.

(1) A factor called DOP (dilution of precision) is a measure of the level of precision that can be expected for a particular arrangement of satellites. The DOP is computed from a number of other factors, including: HDOP (horizontal), VDOP (vertical), TDOP (time). Together these factors are used to compute the PDOP (position dilution of precision). Although PDOP is commonly used, HDOP may be more applicable to DGM work, in which the x,y coordinates are used to map anomalies. GPS accuracy in the vertical dimension is less than in the horizontal. Most GPS receivers can be programmed to output the HDOP or PDOP, which is reported as a number between 1 and 9. For HDOP, a value of 1 is ideal, 2 is considered excellent, 3 to 5 good, 6 to 8 fair, and 9 poor.

(2) Although PDOP (or HDOP) gives some indication of data quality, probably the most important indicator of data quality is the number of satellites used for determining position. It is possible to have a low PDOP and still have significant errors in positioning, especially with few satellites. A minimum of four satellites is needed to determine position; however accuracy increases with additional satellites.

c. Time Synchronization: GPS satellites use atomic clocks capable of extremely accurate time keeping. Geophysical instruments use somewhat less sophisticated clocks, which may drift in relation to the GPS clocks. When recording geophysical data in a separate device from the GPS data, the recorded times are used to later position the readings. It is crucial that the times be synchronized to permit accurate location of the data. Prior to collecting data, the times must be synchronized between the two devices as accurately as possible. When finishing a grid, transect, etc, check the synchronization of the data recorders again, and record any difference noted. The difference will be used to apply a correction to the data.

d. Quality Control: A point will be established on the site where GPS readings will be collected twice daily (AM and PM), for comparison of the computed position. This point will be located in a convenient area, such as the nulling station.

e. Planning Software: Software is available from the major manufacturers of GPS equipment for planning surveys ahead of time. The orbits of the satellites, and the time they will pass over a specific area is included in GPS almanacs, which are downloaded from the satellites by the GPS receiver or may be downloaded from the Internet. The

planning software uses this information to determine the number of satellites and predicted PDOP for a given location and date. At certain times of day, the number of satellites visible to the receiver may be inadequate to provide high quality data. Another possibility is that the constellation geometry may be such that a high PDOP results. In either case, knowledge of this period ahead of time will prevent the consultant from attempting to collect data with poor precision. Work / Rest periods must be planned to avoid data collection in times of poor satellite geometry or few visible satellites.

H Data Storage and Transfer

H.1 Recommended Field Storage and Transfer Procedures.

a. Instrument data should be dumped from the Polycorder, PRO4000 or Allegro to a field computer immediately following completion of a survey grid. If the data logger does not have sufficient memory to complete an entire grid, it will be dumped as needed. Immediate dumping lowers the risk of any data being lost as well as allowing the consultant to make initial assessments regarding data quality and methodology.

b. The field geophysical team should fill out an appropriate Daily Log each day.

I Data Processing and Analysis

I.1 Introduction

This section outlines basic data processing procedures for geophysical data collected for buried munitions surveys. Systematic and proven methods are important to maintain consistent quality of data and to allow for an evaluation of data quality. Identifying and reducing the causes of below standard data is simplified by following a basic established method.

Qualified personnel for data collection and data processing are the most important factors in producing quality data. Data collection personnel should be trained and familiar with the instruments and their operation. Data processing personnel must have an understanding of the geophysical principles and the nature of the data in order to properly evaluate the sensor response. A qualified geophysicist must be able to identify and correct for noise factors and be able to distinguish signals above the noise level. Inexperienced personnel may result in a reduction of the quality or incorrect interpretation of data. The main stages of geophysical data

processing and analysis for buried munitions are field editing, preprocessing, processing and target selection, advanced processing, and the preparation of deliverables.

I.2 Field Editing Data

These steps are performed prior to leaving the site by the field geophysicist or a data processor on site.

a. The software supplied with most Geonics instruments allows the editing of many of the common errors made during data acquisition. A member of the geophysical team, preferably the operator who collected the data, will evaluate the completed file for correctness of line numbers, starting and ending points, and line direction. Fiducial corrections will then be applied to the data. All editing and corrections will then be saved using a new file name.

b. Each line's response amplitude will be examined in profile for overall quality. Particular attention will be paid to geophysical noise levels to ensure that they fall within acceptable thresholds. Acceptable noise levels vary from site to site and should be agreed upon based on the collected data.

c. Once the data file has been edited and checked for quality, it must be converted to a xyz file format for contouring and examination. The most common programs used to contour geophysical data, Golden's Surfer and Geosoft's Oasis Montaj, accept xyz files. Such files can also be viewed as Microsoft Excel spreadsheets.

d. After the data values have been examined and determined to be of expected quality, the positioning of the data must be evaluated. Regardless of whether electronic or conventional navigation methods are used, the process for checking accuracy is the same. Most common contouring programs allow the creation of post maps. These maps show the geographic position of every point collected. The lines and stations should be evenly spaced throughout a grid. Problems in data spacing using conventional navigation methods are usually caused by misplaced fiducial marks or end points and can be easily remedied. Data positioning errors found in electronic navigation can be caused by a variety of problems and are often more difficult to fix.

I.3 Preprocessing

These corrections are applied to the raw data to improve positioning and remove any other errors introduced by the instrument.

a. Incorporating navigation information. Positioning geophysical data and conversion to required coordinate system. When positioning data is stored in a separate file from sensor data, e.g. GPS, a common marker such as a time stamp is required in both data sets to correctly position the sensor data. This step should also include the interpolation of positions, if required, and any conversion or projection to a specified coordinate system.

b. Removal of Instrument Drift and Leveling of Data. Drift correction is needed when the "no response" value of an instrument changes during the course of the survey. This can be caused by temperature variations and may be minimized by allowing the instrument to warm up for a sufficient amount of time before use. Leveling may be performed manually by visual inspection of the data or statistically by calculating the deviation of the data from the mean or "no response" value.

c. Lag (and Offset) Corrections. Lag effects are visible in gridded data as chevron patterns or wavy edges of anomalies, see Figure 9.1. Lag is caused by a time delay in instrument response and the recorded position. Determining the shift is done by measuring the distance between equivalent points of an anomaly on neighboring lines and dividing this value by two. A negative lag will shift the data forward in time (for the sensor trailing the logger) and a positive lag shifts the data back in time (for a sensor leading the logger).

Figure I.1 Example of Chevron Affect

I.4 Processing and Target Selection

This section describes the application of processing routines and filters, analysis of geophysical data and interpretation of gridded or modeled data. When using filters it is important to keep their limitations in mind. Inappropriate usage can result in the removal or corruption of real anomalies, accentuation of noise or ringing, and add errors to the data. An understanding of the effects of filtering is necessary.

a. Gridding and Contouring. Preprocessed data is gridded and contoured to create a smooth interpolated 3D response plot of the area. Gridding method and parameters should be selected to best preserve the true nature of the collected data.

b. Digital Filtering and Enhancement. Data is filtered and enhanced to diminish the effects of noise and enhance the anomalous response and subsequent re-gridding if required. The following list describes some of the more common filters used for geophysical data.

(1) Linear low pass - removes high frequency, short wavelength features from the data. This filter is effective at removing low amplitude high frequency noise and tends to smooth the signal.

(2) Linear high pass - removes low frequency, long wavelength features from the data. The result will be the sharpening of features in the data.

(3) Linear band pass - is a combination of a high and a low pass filter allowing only features with wavelengths between a specified long and short wavelength to remain in the data.

(4) Non-linear - a de-spiking algorithm is effective at removing short wavelength features with high amplitudes from the signal. Filter tolerances are set for the width and amplitude of spikes to be rejected relative to the local background. Once rejected features are removed they can be replaced by interpolated values based on neighboring readings.

(5) Rolling statistics - calculates the statistics within a moving window along a channel of data. This filter will produce a statistical measure of the data within the moving window and outputs the selected statistical value at the center of the window. This

filter can be used as a measure of the variability of the data or as a means to smooth out the appearance of the data.

(6) Difference - useful for identifying noise in data. A difference filter calculates the difference between values in a single channel of data; the fourth difference filter is the most common.

(7) 3x3 Hanning convolution - this smoothing filter tends to reduce low amplitude, high frequency responses within the data. It also improves the appearance of the gridded data by soothing transitions between contours. The overall effect of the Hanning filter is a reduction in the number of peaks within a grid.

d. Threshold Selection. Generally a single threshold is set for an entire site. The selection of the threshold value should be based upon two main factors:

(1) It should be set above the apparent noise level of the data set.

(2) It should be set below the expected response amplitude of buried munition items on the site.

e. Anomaly Selection and Quality Control of Target Picks. A peak-picking algorithm is performed on gridded data to identify anomalies with positive responses above a selected threshold. Any automated target selections must be reviewed by a qualified geophysicist and refined; missed targets should be added and redundant picks removed. If necessary, identify areas or regions that have high ferrous or geologic clutter as it may not be practical to perform discrete target selection within these regions.

f. Prioritization of selected targets. Targets are usually prioritized by amplitude assigned unique target identifiers for each selected anomaly.

I.5 Advanced Processing

Advanced processing involves further steps beyond target selection to prioritize and discriminate selected targets. The items listed below should be regarded as a brief list of the more established advanced processing topics currently being used and developed. There is considerable research being conducted in the buried munitions discrimination field and although

some new methods are producing positive results it is not possible to include a complete list of all developmental processing techniques.

a. Depth Estimates. The Geonics depth calculations used in our software are base on a dipolar approximation. These equations are as follows:

$$\mathbf{d} = -2229.57 + (7288.13 \bullet \mathbf{R}) - (9635.78 \bullet \mathbf{R}^2) + (6458.69 \bullet \mathbf{R}^3) - (2158.63 \bullet \mathbf{R}^4) + (292.118 \bullet \mathbf{R}^5)$$

Equation I.1 Geonics Depth Calculation for 1 x 1 meter system

d is in centimeters

R is the ratio $\frac{TopCoil}{BottomCoil}$

$$\mathbf{d} = -155.95 + (795.09 \bullet \mathbf{R}) - (1715.82 \bullet \mathbf{R}^2) + (2026.38 \bullet \mathbf{R}^3) - (1413.19 \bullet \mathbf{R}^4) + (582.55 \bullet \mathbf{R}^5) - (131.581 \bullet \mathbf{R}^6) + (12.5886 \bullet \mathbf{R}^7)$$

Equation I.2 Geonics Depth Calculation for 1 x 0.5 meter system

d is in centimeters

R is the ratio $\frac{TopCoil}{BottomCoil}$

b. Analysis of Spatial Anomaly Shape. This is used to distinguish between intact ordnance and clutter.

c. Multi-channel Analysis, e.g. Time Decay Curve. Developing systems such as the Geonics EM-63 have shown that different ordnance items have unique responses when viewed over multiple time gates. Currently algorithms are being developed to discriminate different ordnance with this instrument.

SIR® System-2000

Operation Manual

We Provide Complete Survey Solutions

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Chapter 1: Introduction

Unpacking Your System

Thank you for purchasing a GSSI SIR® System-2000 (hereafter referred to as SIR-2000). A packing list is included with your shipment that identifies all of the items that are in your order. You should check your shipment against the packing list upon receipt of your shipment. If you find an item is missing or damaged during shipment, please call or fax your sales representative immediately so that we can correct the problem.

Your SIR-2000 contains the following items:

1 - Digital Control Unit (DC-2A) with software.
1 - Power Adapter (SIR-2000 power connector to a cigarette lighter plug)
1 - Power Adapter (SIR-2000 power connector to an alligator clip)
1 – Retractile Battery Cable
1 – Parallel Data Transfer Cable.
1 - SIR System-2000 Operation Manual

If you purchased some the following available optional items they will also be included:

Portable Battery Kit
T-104 Thermal Pinter

General Description

The SIR-2000 is a lightweight, portable, single channel general-purpose ground penetrating radar system. The various components of the DC-2A control unit are briefly described below.

The major external components of the control unit are the keypad, video screen, connector panel and indicator lights. The keypad consists of 10 keys that are used to control operation of the unit. The VGA liquid crystal display (LCD) video screen provides real-time or playback viewing of the data.

There are five connectors located on the SIR-2000.

- The connector labeled Battery connects to the power supply.
- The connector labeled Antenna connects to a GSSI antenna.
- The Parallel port is used to connect a thermal printer or to transfer data to a computer.
- The Serial port can be used to upgrade the software or to transfer data to a computer not equipped with a bi-directional parallel port.
- The Keyboard connector is used when a standard PC keyboard is needed to reinstall the SIR-2000 operating system.

The red and green indicator lights, located above the power switch, indicate power supply to the unit. The amber light on the upper right indicates hard disk activity.

Powered by a 12 VDC battery, there are two ways that the system can be used, either as a stationary unit or as portable unit to be carried by the investigator. The system is setup and run by the operator via the keypad on the front of the unit. Data can be stored on an internal hard disk drive and optionally printed in real time on a thermal printer. Data is transferred from the system to a computer via a parallel port for post-processing and analysis.

The SIR-2000 can be used with all GSSI antennas from 2000 MHz to 16 MHz. Depending upon subsurface conditions or a building's structural design, this will provide depths of penetration ranging from a few centimeters (inches) to tens of meters (feet). See Appendix B for more details on the antenna selection.

Power Requirements

The SIR-2000 control unit requires a 12 VDC power input at 3 amperes (at the input connector, not at the power source. Note that some loss can occur in the power supply cables). If you purchased a GSSI battery pack to power your SIR-2000, one of the batteries supplied with the pack will be able to power the system for the following periods of time:

4.5 ± 0.5 hours at $40^{o}C$

4 ± 0.5 hours at $20^{o}C$

3 ± 0.5 hours at $0^{o}C$

The above times assume a fully charged battery and GSSI-supplied battery cables. The system can also be powered with an automobile battery or a deep-cycle marine battery. If you power the system from an automobile battery, you should keep the engine running while operating the system, or you will risk depleting the car’s battery to the point where you will be unable to start the engine.

***Caution*:** If you power the system from a vehicle battery, you should keep the vehicle running while operating the system.

If during system operation the input voltage becomes low, the green light above the power button will begin flashing. You should shut down the system as soon as possible and replace or recharge your power source.

Power Indicator Lights

The red and green power indicator lights are above the power button.

Green Light:

- When an adequate power source has been connected to the system the green indicator light will illuminate, even before the system is turned on.
- If the power source is inadequate, the green light will be flashing or not illuminate.
- A flashing green light indicates that the input voltage to the system is less than 10.2v or greater than 18.0v. Check your power source to obtain the appropriate voltage.

- If the input power becomes too low while operating the system, the green light will begin flashing. You should shut down the system as soon as possible and replace or recharge your power source.

Red Light: When the system is turned on, the red light will illuminate.

The battery charger supplied by GSSI with the SIR-2000 (if ordered with your system) has two lights on the front panel.

- One is a power indicator light that illuminates when input power is applied to the unit.
- The other is a "fast-charge" light that will illuminate only during the initial or "fast-charge" phase of battery recharge. When this light goes out, it does not mean that the battery is fully charged, only that the initial or high-current draw phase of the recharge has finished. To ensure that the battery is fully charged, leave it on charge for at least 8 hours.

Operating Environment

The SIR-2000 is designed to operate from 0°C (32°F) to 40°C (104°F). The unit is environmentally sealed and can be used in dusty or humid environments. Though the system is designed to withstand occasional exposure to water it should not be deliberately subjected to rain or immersed in water. A fan provides cooling to the internal components, so make sure that the air intake slots on the left side of the keypad and the small housing on the right side are not covered.

The video screen is a color active-matrix liquid crystal display (LCD) covered by a polarizing screen to improve viewing in bright light. However, even with the polarizing screen, the data can be difficult to view in bright sunlight. Turning the system so that the screen does not directly face the sun will make the data easier to view. Sometimes it will be necessary to completely shade the unit in order to see the image on the screen.

***Note*:** The SIR-2000 is designed to operate from 0°C (32°F) to 40°C (104°F). The SIR-2000 control unit can operate in dusty, humid or foggy environments but it should not be deliberately subjected to direct rain or immersed in water.

Turning the system so that the screen does not directly face the sun and using the sunshade will make the data easier to view in bright sunlight.

The screen on the SIR-2000 is plastic and susceptible to scratching. Reasonable care should be exercised in protecting the screen from sharp objects that may scratch it. Do not use harsh chemicals to clean the screen. We recommend using a soft cloth dampened with clean water.

Chapter 2: Basics Of System Operation

Hardware Connections

Only two simple connections need to be made before you can start the system.

1. The male end of the antenna control cable should be connected to the antenna connector on the SIR-2000 control unit. The 11-pin connector at the other end of the control cable should be connected to a GSSI antenna.

    - Because the control cable connector on the SIR-2000 is different, older GSSI antenna cables will not connect directly to the control unit. You will need to connect the antenna cable provided with your SIR-2000 system to the control unit and connect older GSSI antenna cables to that cable by connecting a cable adapter between the two cables.

Note: If you are going to playback data, it is preferable not to connect the antenna to the SIR-2000 before powering ON the system.

2. The male end of the DC power cable should be connected to the battery connector on the control unit.

The following connections are for optional items:

a) If a thermal printer is to be used, the male end of the thermal printer cable should be connected to the parallel connector of the control unit and the other end should be connected to the printer. See Chapter 6 for details on using thermal printers.

Caution: If you connect a printer to the SIR-2000, the printer must be powered ON before the SIR-2000.

b) If a survey wheel is to be used, connect the survey wheel to the antenna.

After all other connections have been made connect the power cable to the power source.

- If the battery voltage is adequate, the green light above the power button will become illuminated and remain illuminated.
- If the battery voltage is low the green light will flash. If the green light is flashing you should correct the low voltage problem before starting the system.

Caution: If the battery voltage is low, the green light above the power button will flash. If the green light is flashing, you should correct the low voltage problem before starting the system.

System Startup

This section will describe the initial sequence during startup.

1. Pressing the Power button in the top left corner of the SIR-2000 will turn ON the system. After power up both the green and red lights above the power button should be illuminated. If

the green light is dark and the system will not power ON, you have inadequate input power. Check your power source.

***Note*:** If the green light is dark and the system will not power ON, you have inadequate input power. Check your power source and connections between your power cables.

2. The SIR-2000 will show a series of DOS messages during the start-up sequence.
3. Next, the SIR-2000 Radar Control Unit opening screen will appear showing the version of the operating system software.
4. At the bottom of the screen you are given the following choices:
   - Press the Run key for Automatic operation - see Chapter 9.
   - Press the Enter key for Standard operation.
5. At this point, we will press the Enter key and initiate Standard operation. When the Enter key is pressed, the following message appears at the bottom of the screen:

   Press: the Left Arrow key for Previous Setup or the Right Arrow key for Stored Setups

If you choose Stored Setups, a list of system operating parameters setup files will be displayed on the screen. Many of these files are GSSI custom files for easy setup of the various GSSI antennas. (For a description of the contents and selection of the various parameter setup files see Appendix A).

- Use the Arrow keys to highlight the name of the setup file you wish to recall.
- Press the Enter key to recall the setup file and set the system. A second screen will appear asking you to confirm the recall.
- After the system is set you will be in the Collect Setup Menu block. If there is no antenna connected to the system, and you try to recall a setup file, the message “No Data Available” will appear on the screen.

If you choose Previous Setup, the system will recall the same operating parameter settings as the last time it was used. It will then enter the Collect Setup Menu block.

If an antenna is not connected to the system and you choose Previous Setup, the system will enter the Playback Setup Menu block. See Chapter 5 for a description of the Playback Setup Menu block. If you accidentally choose Stored Setups, press Enter and then Cancel. The system will then enter the Playback Setup Menu Block.

6. Once in the Collect Setup Menu block, data coming from the antenna will show on the top left ¾ of the screen, and oscilloscope display of the data in the top right ¼ of the screen and the bottom portion of the screen will show the Collect Setup Menu block. Note that the data being acquired at this time is only displayed to the screen and it is **not** saved on disk.

Review the remainder of Chapter 2 for a general description of how to use the system, then go to Chapter 3 for system data collection parameters setup.

Using The HELP Key To Get Help

Highlight any menu command and then press the ?(Help) key to get help on that command. Press the Help key and then the Enter key to get general help on the system. Help for some commands is longer than one screen, and in these cases use the Down arrow key to obtain the additional screens of help.

***Note*:** General system help can be obtained by pressing the Help key and then the Enter key. If at any time you are unsure of the current system parameter settings press the Collect/Playback key until the system parameters screen appears.

The Operating Keys

The SIR-2000 is operated via a scrolling menu system which is controlled by nine keys. There is also a power ON/OFF key. This section describes the function of the operating keys and the three indicator lights on the top of the system.

Power Key : This key is used to turn the system ON and OFF. If power is accidentally disconnected, an internal battery supplies adequate power to ensure that the current disk file is properly closed.

Red And Green Power Indicator Lights:

- When the system is connected to an adequate power source, (whether the system is turned ON or OFF), the green light will illuminate steady.
- If the power source voltage is low, the green light will flash. If the green light is flashing, you should not turn the system ON.
- When the system is powered ON, the red indicator light should illuminate.
- The green light will begin flashing during operation if the voltage drops below acceptable levels.

? (Help)Key : Highlight any menu command and then press the ?(Help) key to get help on that command. Press the Help key and then the Enter key to get general help on the system.

Print Key : This key is used in conjunction with the Select Block command to produce snapshot prints of the data.

Collect/Playback Key : This key is used to toggle the system between Collect Setup Mode, Playback Setup Mode and the Setup Parameters screen.

Enter Key - This key is used to toggle through options of menu parameters surrounded by a box, and to accept parameter value changes.

The Arrow Diamond : This arrow diamond is used to move around the menu columns. It is also used to change the values of parameters where appropriate. When in Collect Data Mode, and the system is scanning, pressing the Up arrow will generate location markers in the data.

Run/Standby Key :

- When in Collect Setup Menu block, this key starts the system collecting data.
- When the system is collecting data, pressing this key will pause data collection.
- When the system is collecting data, pressing this key and holding it for 2 seconds will stop collecting data and close the file.
- When in Playback Mode, pressing this key will start playback of the selected file(s).
  - Press the key a second time to pause data playback.
  - When paused, press again to resume playback.

The Amber HDD Indicator Light: When the hard disk is active reading or writing data, this light is illuminated.

Navigating Through The User Menus

The Major Menu Blocks

The SIR-2000 has four major menu blocks:

- Collect Setup
- Playback Setup
- Playback Data
- Collect Data

The system will identify which block is active by a message appearing in the lower portion of the menu block.

Setup Menu Blocks

When the system is first turned ON, it is in Setup Mode. When in the Setup Major Menu block, pressing the Collect/Playback button cycles through the major menu blocks; Collect Setup and Playback Setup, and the Current System Parameters screen (Figure 1).

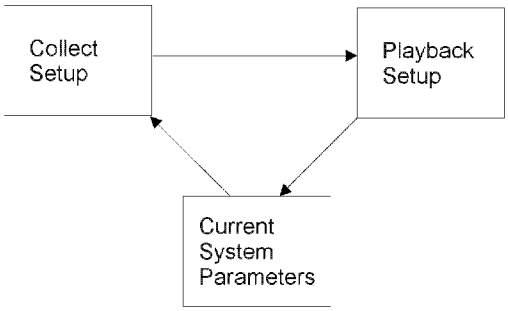


Figure 1: Cycling through the major menu blocks when in Setup Mode by repeatedly pressing the Collect/Playback key

Collect Data And Playback Data Menu Blocks

To put the system in Data Mode, press the Run/Standby key. This will start the system collecting data Note: By default the data will be stored in RAM. It will only be stored on the hard disk if you turn disk output ON.

In the Data Mode, pressing the Collect/Playback button cycles through the major menu blocks; Collect Data and Playback Data, the current system parameters screen and then the Collect Setup Menu Block (Figure 2).

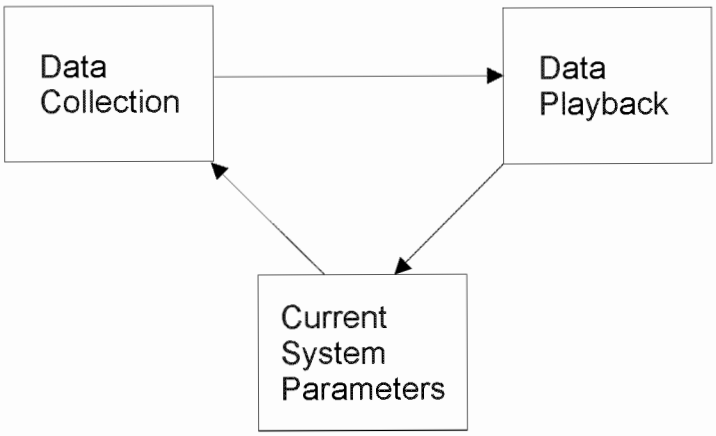


Figure 2: Cycling through the major menu blocks when in Run Mode, by repeatedly pressing the Collect/Playback key.

To return the system to Setup mode, select Go To Setup from the first menu column.

Note: When the SIR-2000 is first turned ON it is in Setup Mode.

To put the system in the Data Menu block, press the Run/Standby key. When in a DATA MENU block, to return the system to setup mode, select Go To Setup Mode from the first menu column.

Caution: Data stored to RAM will be lost when the system is powered OFF or when the next data file is collected. To permanently save your data, you must set the Disk Output Parameter to ON.

Using The Menus

The menu palette is prioritized from left to right. The left-most column of commands is referred to as the first column, the next column to the right is referred to as the second column, etc. The currently highlighted item is the active item. The user can navigate between items using the Arrow keys. To select and activate a command move the highlight bar to that command and press the Enter key.

- The left-most column consists of super commands that, when selected, bring up a list of commands in the second column.

- The middle columns consist of two types of system parameters: those whose values appear in a box and can be changed via the toggle switch method and those whose values can be changed by a parameter change box.

  When a parameter from these columns is highlighted and then the Enter ↵ key is pressed, one of two things will happen:

  - If it is a toggle switch parameter, the value of the parameter will change each time Enter ↵ is pressed.

  - if the parameter requires a wide range of values a parameter change box will appear as a third column. The Up ↑ and Down ↓ keys will be used to increment/ decrement value of the parameter by the step size; the Left ← and Right → keys will allow you to select step size. The Enter ↵ key will set the selected value of that parameter.

Note: Throughout the remainder of the manual when the expression "select a command" is used, it means move the highlight bar to illuminate that command and then press the Enter ↵ key. This will select (i.e., activate) that command.

Let's look at some examples of using the menus.

1) Playback Setup menu block, if you highlight the Files command from the leftmost column a list of commands will appear in a second column.

2 Now, using the Arrow ← ↑ ↓ → keys move to the second column and highlight the Compress command. A third column containing two compression commands appear, Method and Do Compress.

3) Finally, if you move the highlight bar to the Method command and press the Enter ↵ key three times slowly. Notice that this changes the type of compression method.

4) In the Collect Setup Menu block move the highlight bar to the Setup command and then to the Range command. Notice that a parameter change box appears to the right. Move the highlight bar to the Parameter Change box to change the value of the range. Then press the Enter ↵ key to register the change.

Recalling Preset Files To Automatically Set The System For Data Acquisition

When the system is first turned ON or after switching antennas, the system can be easily set for data acquisition by selecting the operating parameters setup file that is most appropriate for the selected antenna and job. This is done using the Recall Setup command accessed from the Setup command in the Collect Setup Menu block or the Playback Setup Menu block. This command is next to the bottom of the second column of commands.

Recall Setup

This command allows you to setup the system by recalling a file of previous system settings. See Appendix A for a detailed description of all the GSSI preset parameter setup files.

1. When this command is highlighted and the Enter key pressed, a list of 29 factory preset and 56 user-definable setup files will be displayed on the screen.
2. Use the Arrow keys to highlight the name of the setup file you wish to recall.
3. Press the Enter key twice to recall and confirm the setup file you want to configure the system.

Show Setup

This command will display the current system settings.

Chapter 3: System Setup For Data Collection

Simple (Quick) System Setup For Data Collection

After loading the appropriate system operating parameters setup file (see Appendix A for a description of the setup files), the following few parameters should be checked to ensure that they are optimal for your specific site.

The system should be in the Collect Setup menu block.

Step 1: Check the Range (i.e., depth) of viewing.

This is done by moving the highlight bar up to the Range parameter. The appropriate range value is calculated by the following formula:

RANGE VALUE = Maximum Depth of Interest * T * 1.5

Where T is the two-way travel time of the subsurface materials at your site. For a table of two-way travel time values see the discussion of range in Section Setting the Data Acquisition Parameters.

After the range value is changed, the system will automatically find the position of the ground surface reflection and place it at the top of the data screen. It will also readjust the gains (the message "servo in progress, please wait" will appear, and the speaker will emit a “clicking” sound while this is occurring).

Step 2: Check the position of the ground surface reflection.

Normally, the surface reflection will appear in the color bar at the top of the O-scope data display. Occasionally the system will misidentify a different reflection for the ground surface reflection. (It is especially prone to do this with the horn antennas, 1000 MHz antenna, 3200 MLF antenna, bistatic 100 MHz and the bistatic 300 MHz antenna.)

In this case, the real surface reflection will occur before the top of the signal (as displayed in the O-scope display).

1. Move the highlight bar down until the Position command is highlighted and press the Enter key to change position to Manual Mode.
2. Move to the parameter change box and use the Down arrow to decrease the position value by 5ns if the range is less than 20ns, by 10ns if the range is between 20ns and 100ns and by 50ns if the range is greater than 100ns. (Note that when changing the position value the system will often round off values.)
3. Before you change the position value you should note the original value.
4. Press the Enter key to implement the position change.

After changing the position value, you will observe one of two things:

1) If the oscilloscope display shows the data is flat (no signal) at the top and a strong surface reflection appears further down, the system correctly found the surface reflection. Move the

highlight bar to the Parameter Change box again and set the position value back to the original number before you changed it.

2) If the data is not flat at the top of the record the wrong surface position was found. You should keep manually decreasing the surface position by increments of 5 or 10ns until the data is flat at the top. At that point you will have correctly found the surface position.

Step 3: Check the Gains to ensure proper signal amplification.

If the gains are set correctly, the largest signals (i.e., reflections) in the oscilloscope display should be 75% the width of the display and the data screen should show mostly (60% to 80%) red, orange and yellow reflections (using the default Color Table 2 And Color Transform 1). If you use a different color table or transform the above colors will not apply.

If the gains values are too low, a significant (> 25%) portion of the data reflections will show as black and grey (low signal). In this case increase the value of the gain point(s) associated with the low signal zone, until the signals in that zone are red and orange. The time markers to the left of the oscilloscope display correspond to the gain points. Thus, the time label at the top of the screen is gain point 1 and the next time label is gain point 2, the next time label is gain point 3, and so on. The number of time labels is the same as the number of gain points. Therefore, if the top of the display has low amplitude you should increase the value of gain points 1 and 2.

The gains are changed by changing the Gain parameter to manual by pressing the Enter ↵ key and then changing the values of individual points.

Step 4: Check the Run Mode (i.e., data collection method).

- If you will be collecting data continuously along survey lines, then Run Mode should be set to Cont.
- If you will be using a GSSI survey wheel to control data collection, Run Mode should be set to SW. You must calibrate the survey wheel before using it!
- If you will be collecting data at discrete data points along the survey lines, set the Run Mode to Point.

Step 5: Check your output devices.

Go to the Output Menu item and check to ensure that Disk is ON.

If you want to use a thermal printer to make real-time printouts of your data, set Print to ON. Note - there will be a long delay here (about a minute) if the printer is not connected and powered ON, the speaker will sound and the screen will display a window that says “Plotter error - Hit any key to continue.” If you press the key more than once, the delay time will stack up.

Step 6: Check the Display Mode.

- By default the display is Color Linescan.
- If you want to change to Linescan grayscale, Wiggle trace or Oscilloscope display change the Display Parameter.

Step 7: Press the Run/Standby key to begin collecting data. This will start the data collection and place the system in the Collect Data Menu block. See Chapter 4 for further details on data collection.

Complete Description Of Collect Setup Menu Block

Setup

When this command is highlighted, a set of system data collection parameters that can be set appears in the second column. The commands that will appear in the second column are: Setup Mode, Run Mode, Range, Gain, Position, Filters, Scan, Save Setup, Recall Setup, and Show Setup.

Setup Mode

This parameter determines how the system parameters will be set. There are two setup modes: Automatic and Manual, which are changed by pressing the Enter key.

- When the Setup Mode is set to Automatic, the system will automatically find the direct coupling and place it at the top of the screen, set the filters, gains, scan speed and data resolution. It will not automatically set the range. The range used will be that which is set prior to putting the system in Automatic Mode. After automatic setup the user can manually change any system settings.
- When the Setup Mode is set to Manual, the user can manually set all system parameters to the desired settings.

Caution: When the Setup Mode is set to Auto, the Gain Position, Filters and Scan Parameters will be hidden.

Setting The Data Acquisition Method

Run Mode

This parameter informs the system how the field survey will be conducted. There are three methods of data acquisition: Cont (continuous), Point and SW (survey wheel). The system Run Mode is changed using the Enter key.

Continuous Data Collection Method: When the Run Mode is set to Cont (Continuous), the system is continuously transmitting signals into the ground and recording data. The advantages of this mode are that a continuous profile of the subsurface is generated and it is the most rapid data collection method.

Survey Wheel Controlled Data Collection Method: When the Run Mode is set to SW (Survey Wheel), a third column of survey wheel data collection parameters appears. In this mode, data collection is controlled by a survey wheel attached to the antenna. All lines will then have the same horizontal scaling. This mode is preferable for surveys that require precise line locations.

- **Units**: This parameter is used to set the survey units. Use the Enter ↵ key to switch between meters and feet.
- **Scans/Unit:** The Scans Per Unit parameter sets the horizontal sampling along the ground that is controlled by the survey wheel. The larger the value for the scans/unit, the more often the radar will scan the ground.
  - For concrete surveys with the 1000 MHz or 900 MHz antennas, a setting of 40 scans/unit is typical.
  - For near surface (1-3 meters) utility surveys with the 500 MHz or 300 MHz antennas, a setting of 20 scans per meter is normal.
  - Often for large-scale surveys (i.e., bedrock mapping) a coarser horizontal sampling is desired and settings of 1 to 10 scans per meter are typical.
  - Sometimes surveys are done pulling antennas with a vehicle at a higher rate of speed (ex. 2-5 meters (6-15 ft) per second). In these cases, settings of 0.1 to 1 scans per unit are typical.
- **Units/Mark:** This value determines how often distance marks are placed on the data display.
  - Typical values for concrete and near surface surveys where high horizontal resolution is critical are .1 (marks every 10cm) to .5 (marks every 0.5 meters).
  - Typical values for utility surveys and deep stratigraphic surveys are 0.5 (marks every 0.5 meters) to 5.0 (marks every 5 meters).
- **Dir**: This is the direction of the survey wheel rotation. If it rotates clockwise, when viewed from the same side as the encoder, choose Forward; counterclockwise, choose Reverse. If you are unsure, use Auto. When the survey wheel is calibrated, the direction is automatically sensed and set to the appropriate direction (i.e., same direction as calibration run). After calibration, the wheel direction will be automatically sensed by the system, increasing survey efficiency and making tasks such as pipe location easier.

Note: The Survey Wheel must be calibrated at your survey site before use.

- **Survey Wheel Calibration:** Survey wheel calibration is done by selecting the command SW Calibr. A list of survey wheel calibration commands will then appear in the right column.
- **Auto Calibr:** You must calibrate the survey wheel before each survey. You should perform the following steps to autocalibrate the survey wheel for your site:

1. Choose a survey wheel calibration line that is at least 50% as long as your maximum survey line. Enter the distance of the survey calibration line in the distance parameter.
2. Select the survey units either meters or feet.
3. Set the antenna at the beginning of your survey calibration line with the middle of the antenna on the beginning of the line.
4. Activate the Autocalibrate function by pressing the Enter ↵ key and then the Run/Standby key.

5. Move the antenna over the survey calibration line very slowly (less than 0.5meters (1.5ft) per second), until the middle of the antenna reaches the end of the survey calibration line.
6. When finished calibrating, press the Run/Standby key to end the calibration.
7. Your survey wheel is now calibrated and ready for use.

- **Units:** Use the Enter key to select the survey units Meters or Feet.
- **Distance:** Enter the distance of the survey wheel calibration line. The distance should be at least 50% of the longest line in the survey to be performed.

Tick/Unit: If you know the number of electronic ticks per meter or feet that your survey wheel will send to the SIR-2000 system, you can enter the number here. With this number it is not required to calibrate the survey wheel.

We strongly recommend using the Autocalibrate function instead of entering a tick/unit value, because ground conditions change and when the system is Autocalibrated it will take this into account to some extent.

Discrete Data Point Data Collection Method: When the Run Mode is set to Point**,** the parameter Stat Stack appears in the third column. When in Point Mode, data is collected a predetermined number of scans per survey station (i.e., every time the Run/Standby key is pressed another number of scans are collected).

This mode is useful in rough terrain where continuous data collection is impossible and in areas where the signal is very weak at deep depths and maximum signal enhancement is required. When using Point Mode, it is recommended that Wiggle Display Mode be used.

Be aware that the display shows a simulated stack while in Collect Setup. The system shows the actual stack when switched to Run Mode and you start acquiring data.

Stat Stack: In order to improve signal-to-noise in Point Mode, it is advantageous to stack (i.e., average) several input scans into one output scan at each station. The Stat Stack parameter allows you to set the number of scans that will be averaged.

The value is typically set to 32, and the range is from 1 to 32768 in binary steps. Thus, when the value is set to 32 at each station, 32 scans will enter the system from the antenna and be summed into one scan. The resulting scan will be output to the video screen and stored on disk. If the data is of poor quality during your test lines, try increasing the value of Stat Stack**.**

Setting The Data Acquisition Parameters

Range

The Range parameter is a time value in nanoseconds. When you set the range to a value, (for example: 10 nanoseconds) this tells the system how long to record received reflected signals after it sends out a radar pulse. Any portion of the radar pulse which can penetrate into the ground, reflect from an object or boundary and return to the antenna within 10 nanoseconds is recorded and displayed (this record is termed a scan).

When the system is set to record for 10 nanoseconds, signals cannot penetrate very far into the earth and return within 10 nanoseconds. However, if the range is set to 100 nanoseconds, signals

can penetrate much further into the ground and return to the antenna within 100 nanoseconds. You have effectively increased your depth of viewing.

Note that for a given antenna frequency at a given site, there is always a maximum depth into the ground that the radar signal can penetrate. There is some maximum range value for any given situation beyond which you will get no signal. ***Ground penetrating radar signals will not travel through metal or salt water***.

The range value to set, for your particular job, is determined by the following formula:

$$RANGE = D \times T \times 1.5$$

where,

D - is the maximum depth of interest

T - is the two-way travel time of the subsurface materials. This is the time it takes for the radar wave to travel down and back through one meter (or foot) of a particular material. For your particular site, make the best determination of what the particular subsurface material is and refer to Table 1 below to obtain an estimate for the two-way travel time. This value can then be used in the formula above to determine the proper range setting.

Warning: the two-way travel time values are only estimates. The exact two-way travel time at your site will likely vary somewhat from the estimated values.

TABLE 1

Approximate two-way travel time values of various materials

Material	T (ns/meters)	T (ns/feet)
Air	6.5	2
Ice	13	4
Snow	8	2.5
Water	59	18
Asphalt	14	4.5
Dry concrete	15	4.5
Wet concrete	23	7
Dry sands	13	4
Wet sands	25.5	7.5
Saturated sands	33	10
Dry sand & gravel	15.5	4.5
Frozen sand & gravel	14.5	4.5
Dry loamy/clayey soils	10.5	3
Dry mineral/sandy soils	16	5
Organic soils	52.5	16
Wet sandy soils	32	9.5
Frozen soil/permafrost	16	5
Tills	22	6.5
Peat	51.5	15.5
Wet clay	34	10.5
Dry clay	13	4
Dry granite	14.5	4.5
Wet granite	16.5	5
Wet basalt	19	6
Volcanic ash	23.5	7
Potash ore	15	4.5
Dry bauxite	33	10
Syenite porphyry	16	5
Travertine	18.5	5.5
Coal	14	4
Dry limestone	15.5	4.5
Wet limestone	18.5	5.5
Wet sandstone	16	5
Dry salt	16	5

Estimating The Depth Of A Target

To estimate the depth of an object or layer on the radar record, with the system in Standby, enter the Cursor Mode (from the Collect Data Menu Block) and measure the two-way travel-time to the target.

This is done by moving the horizontal cursor line until it aligns with the top of the object; the two-way travel-time is the Y value in nanoseconds (ns) at the bottom of the screen. Divide the two-way travel time by your estimated two-way travel time value from the Table 1 above and the result will be an *estimate* of the depth to the object or layer.

Alternatively, if the VERT SCALE=DEPTH, the cursor will read the depth directly (provided the dielectric value is set properly).

Gain

The signal from the antenna that enters the SIR-2000 is very low amplitude and must be amplified by the system for viewing and interpretation. The amount of amplification necessary depends upon the subsurface conditions at the particular site and varies from site to site. The gain function (curve) is equal to the amount of amplification the SIR-2000 applies and can be set to provide the best amplification for data presentation at the site you are working on.

The gain parameter can be set to Auto or Manual using the Enter ↵ key. When set to Auto**,** the system will automatically set a gain function based on the data input. When in Manual Mode, the user can manually change the gain function. When this is set to Manual**,** the gain point values appear in the third column and can be adjusted.

Since reflections from greater depths require more amplification, the amount of amplification increases with depth. Thus, the SIR-2000 applies what is called a time-varying gain (TVG) curve. The number of points used to define the curve is controlled by the user and can vary from 1 to 8. The use of 3 to 5 gain points is typical.

When manually adjusting the gain curve, the gains are set correctly when the largest signals (reflections) in the oscilloscope display are 75% the width of the display and the data screen shows mostly (60% to 80%) red, orange and yellow reflections. The colors described above are based on Color Table 2. If you use a different color table the correct gain colors will be different, but the same principle applies.

If the gains values are set too low, a significant (> 25%) portion of the data reflections will show as black and gray (low signal). You should increase the value of the gain point(s) associated with the low signal zone, until the signals in that zone display red and orange. The time markers to the left of the oscilloscope display correspond to the gain points. The time label at the top of the screen is gain point 1 and the next time label is gain point 2, and the next time label is gain point 3, and so on. The number of time labels is the same as the number of gain points.

***Note*:** When manually adjusting the gain curve, if the gains are set correctly, the largest signals (reflections) in the oscilloscope display should be 75% the width of the display and the data screen should show mostly (60% to 80%) red, orange and yellow reflections. The colors described above are based on color table 2. If you use a different color table the correct gain colors will be different.

Gain Points: The number of gain points can be set from 1 to 8, and is normally set between 3 and 5. You may want to use fewer gain points (2 or 3) for shallow scans (5-15ns) made with our high-frequency, high resolution antennas for detecting steel reinforcing bars or mesh in concrete. Conversely, you may want to use more gain points (6 or 8) to allow greater adjustment flexibility when doing deep investigations (200-1000+ns).

Position

This parameter controls the vertical position of the surface reflection in the data viewing window. The surface reflection is the place in time where the radar pulse leaves the antenna, and enters the subsurface. It can therefore be considered to be "time zero", and its position should be at the top of the scan.

- When Position is set to Auto Mode, the system will attempt to identify the surface reflection and place it at the top of the data viewing window. The surface reflection is always a very strong reflection. The gain parameter should be set to Auto when using the Auto Position.

  Note that the ability of the system to correctly identify the surface reflection depends upon the antenna selected and the ground conditions. It is important to check that the system has correctly identified the surface reflection.

  This is done by manually moving the scan down the viewing window by decreasing the range by a few nanoseconds. If the Auto Position has correctly identified the surface reflection, these data should be a nearly flat line (no signal) at the top of the scan above the surface reflection as you move the scan down the viewing window. If, as the scan is moved down the viewing window, more data appears above, then the Auto Position has not found the surface reflection. You should continue to move the scan down the window until the data becomes a nearly flat line at the top of the screen. The large reflection just below the flat data zone will be the surface reflection. The gain should be set to Manual when manually adjusting the scan position.

- To manually move the data scan up or down in the window, set Position to Manual. A fourth column will appear which will allow you to move the scan. The Step parameter controls how much the scan is moved up and down and is changed using the Right → and Left ← arrow keys.
  - Use the Up ↑ arrow key (increase time in ns) to move the data scan up in the window.
  - Use the Down ↓ arrow key (decrease time in ns) to move the data scan down in the window.
  - Gain should be set to Manual when manually adjusting the position.
  - When using Manual signal position, keep the gains at a minimum when searching for the transmit pulse.

Filters

The Filters command can be set to Auto or Manual by highlighting the command and pressing the Enter ↵ key.

- In Auto Mode the system estimates the center frequency of the data and sets the Vert HP (vertical high pass) filter to a frequency three octaves below and sets the Vert LP (vertical low pass) filter to a frequency one octave above the center frequency. The Hor Smooth filter is set to 3 scans and the Hor Bkgr RM is turned OFF.
- Setting the Filters to Manual Mode cause a third column of filter parameters to appear, these are Vert HP, Vert LP, Hor Smooth and Hor Bkgr RM.

***Note*:** If you select a parameters setup file for your antenna, the filters will automatically be set and you should not be concerned with changing them unless you change antennas.

Vert LP: The Vert LP (vertical low pass) filter is used to eliminate high frequency noise (which appears as "snow") from the data. When this parameter is highlighted, a fourth column appears which allows you to set the value of this filter. The Vert LP filter is defined in terms of frequency in MHz.

The value of this parameter should be set according to the following formula:

VERT LP = ANTENNA CENTER FREQUENCY * 2

As the value of this filter is decreased, more filtering occurs and more data will be removed by the filter. This is a three-pole IIR (Infinite Impulse Response) filter.

Vert HP: The Vert HP (vertical high pass) filter is used to eliminate low frequency noise (e.g., tilt) from the data. When this parameter is highlighted, a fourth column appears which allows you to set the value of this filter. The Vert HP filter is also defined in terms of frequency in MHz.

The value of this parameter should be set according to the following formula:

VERT LP = ANTENNA CENTER FREQUENCY / 6

As the value of this filter is increased, more filtering occurs and more data will be removed by the filter. This also is a three-pole IIR filter. This filter **MUST** always be set when collecting data.

The Hor Smooth (horizontal smoothing) process filters the data horizontally, eliminating random noise and smoothing the data. This is an IIR running average filter and can help emphasize continuous layers. When this parameter is highlighted, a fourth column appears. The input value is number of Scans**.**

This filter is normally set to a value of 3. As the filter value is increased, more smoothing occurs and smaller targets are smoothed out of the data. If conducting rebar or utility surveys this filter should be set no greater than 5. If you are looking for very small objects in the near subsurface (like wire mesh reinforcing in concrete), you should turn this filter off by setting it to zero. For subsurface layer mapping the value of this parameter may be increased but is normally less than 20.

Hor Bkgr Rm: The Hor Bkgr RM (horizontal background removal) filter is used to improve the recognition of small targets and dipping reflectors.

This process filters the data horizontally by removing horizontal noise bands and reflecting layers. This filter **SHOULD NOT** be used in Data Collection Mode because it removes the surface reflection and any other real horizontal reflections.

When this parameter is highlighted, a fourth column appears. The input value is number of Scans. This is an IIR (infinite impulse response) running average subtraction filter. The filter works by taking an average of the data and subtracting the average from each scan. The smaller the selected filter value the more effect the filter has.

This filter is best used in playback when looking for point targets and there are significant horizontal noise bands. Use the Cursor to measure the width in terms of the number of scans of the largest point target and set the Hor Bkgr RM filter to this value. The filter will remove all horizontal banding that is equal to or longer than the set value of this parameter, provided there is no change in amplitude or depth of these horizontal signals.

Scan

This menu item sets the parameters of the data scans. These parameters are samples/ scan, bits/sample and scans/second. Scan can be set to Auto (automatic) or Manual using the Enter key.

When in Auto Mode, the parameters are automatically set by the system. The samples/ scan will be set to 512, the bits/sample to 8 and the scans/second to 32, unless factory setups have been chose. In this case, the samples/scan and bits/sample may differ.

When in Manual Mode, the parameters, samples/scan, bits/sample and scans/second appear in the third column. The user can now manually set these parameters.

Samp/Scan: This parameter sets the number of data samples in a vertical scan. When it is highlighted, a fourth column appears which allows you to change the value of the parameter. The samp/scan can be set to 128, 256, 512, 1024, or 2048.

This value is normally set to 512 samples/scan, which is the best value for most applications. However, for each antenna frequency there is a maximum value that the range should be set when recording 512 samples/scan and occasionally you may wish to set the range beyond this value. In this case you must increase the samples/scan to a higher value, otherwise your data will be under-sampled or aliased (i.e., resolution will be lost).

This maximum permissible range when recording 512 samples/scan is calculated by the following formula:

Maximum Range = (512 * 100) / (Antenna Center Frequency)

where the antenna center frequency is in Megahertz. For example, using the 500 MHz antenna:

Maximum Range = (512 * 100) / 500 = 102 nanoseconds

If using the 500 MHz and you decided to set the range beyond 102 nanoseconds, then the samples/scan should be increased to 1024 or 2048 if necessary.

The maximum permissible range for any given antenna and samples/scan (SS) value is calculated by:

Maximum Range = (SS * 100) / (Antenna Center Frequency)

One more example: For a 100 MHz antenna and 1024 samples/scan the maximum permissible range would be:

1024 nanoseconds = (1024 * 100) / (100)

If you wish to conserve disk storage space, you may wish to record 256 or 128 samples/scan. However, you must use the maximum range formula to ensure that you are not under-sampling your data. **Always** set your range first, then decide if you can use less than 512 samples/scan.

Bits/Sample: The Bits/Sample parameter can be set to either 8 or 16 by toggling the Enter ↵ key.

The number of bits determines the dynamic range of the data. Data recorded at 16 bits has better dynamic range (i.e., the data can discriminate between two reflectors of small amplitude differences), but this will use twice the disk storage as 8 bit data.

- If your survey objective is to find high amplitude targets such as metal, voids or highly reflective layer you should set Bits/Sample to 8. This will provide adequate dynamic range and save disk space.
- If your survey objective is to map the various layers of the subsurface and they have a wide range of amplitudes, **and you plan on post-processing the data on a computer, you should set the number of bits to 16.**

Scans/Second: This parameter controls the horizontal sampling rate along the ground when the system is in Continuous Mode. When Scans/Second is selected, a fourth menu column appears which will allow you to change the value. The possible values of this parameter depend upon the samples/scan setting selected. You should always set the Samples/Scan before the Scans/Second.

Samples/Scan Setting	Scans/Second Choices
128	16,24,32,48,64
256	16,24,32,48
512	16,24,32
1024	16,24
2048	16

The normal setting is 32 scans/second. When surveying on foot at approximately 1 meter (3 feet) per second, a setting of 32 scans/second will result in a data scan about every 3 cm (1 inch) along the ground surface. If you wish to increase your scan density, you should walk slower. For example, a walking pace of 60 cm (2 feet) per second will result in a data scan approximately every 2 cm (1 inch) along the ground surface.

Often for large-scale surveys (i.e., bedrock mapping), a coarser horizontal sampling is desired (ex. scans every 20 cm (8 inch)). In such cases, the scans/second value can be lowered to 24 or 16. This will result in smaller files, saving disk space and speeding up data transfer and post-processing.

Sometimes surveys are done pulling antennas with a vehicle at a higher rate of speed (ex. 2-5 meters (6-15 ft) per second). If a setting of 32 scans/second does not provide adequate horizontal

sampling, you may increase the scans/second setting to 48 or 64. Note that scans/second settings of 48 and 64 are generally only available when the samples/scan are set to 128 or 256.

Setup Of Disk, Printer And Display Output Parameters

Output: When this command is highlighted, the Output Setup commands appear in the second column.

Pressing the Enter ↵ key when Output is highlighted will have no effect.

Disk: The hard drive storage device can be operated by highlighting the word Disk in the menu in the second row and toggling the Disk On or Off with the Enter ↵ key.

- If Disk On is selected, data will be stored to the hard disk, and the message "Out:D" will appear in the lower right corner of the screen. Each filename consists of the word FILE + a number (ex. FILE8), where the number increments for each file saved.

Print: This function turns the print output ON or OFF by using the Enter ↵ key. When it is turned ON, a third column of printer control commands appears. If the printer is not connected and turned ON, there will be a long delay (about a minute) when this parameter is selected.

Printer: Use this command to select the printer you will be using to print the data. The Enter ↵ key is used to toggle between the supported printers.

Horizontal Zoom: This parameter stretches the data printout in the horizontal direction. The possible values are 1, 2, 3, or 4 and the Enter ↵ key is used to change the value.

A value of 1 means that each scan of a data file is printed as one scan on the printer. A value of 2 means that each scan of a file is output as 2 duplicate scans on the printer. A value of 3 means that each scan of a file is output as 3 scans on the printer and a value of 4 means 4 scans are printed for each scan in a data file.

When in Linescan Mode, the T-104 and the GS-608P print 203 scans per inch. The SIR-2000 video display displays 94 scans per inch. A horizontal zoom setting of 2 will give the best match between the video screen and the printout.

Orientation: This parameter controls the orientation of the data as it is printed on the paper. The orientation can be Normal or Flipped (vertically) and is changed by pressing the Enter ↵ key.

In the Normal setting the top of the data will print at the top of the paper. In the Flipped setting the top of the data will print at the bottom of the paper.

This is useful when adjacent survey lines are collected in opposite directions. When the direction of data collection is reversed and the data printout is set to Flipped, you will be able to easily align all the printouts and compare adjacent features. For example, if the odd numbered survey lines (1,3,5,7...) are collected from East to West and printed Normal, and the even number survey lines (2,4,6,8...) are collected from West to East and printed Flipped, you will be able to align all printouts and compare features.

***Caution*:** The Scans/Second parameter must be set to 32 or less when printing data during acquisition. The Horizontal Zoom must be set to 1 when printing data during acquisition.

Display: This command controls how the data is displayed to the video screen. There are three types of data display; Linescan, Wiggle, and O-Scope. Use the Enter key to toggle through the three types of displays. When the display type is changed, the appropriate display parameters to be set appear in the column three.

- Using the Linescan display, the reflected radar signal is mapped by amplitude and polarity to different colors or shades of gray. A color scale of 16 colors is used. Eight colors represent positive amplitudes and eight colors represent negative amplitudes. Each level of signal in a scan is assigned a color depending upon its amplitude. Each scan results in a vertical line of colored (or gray-shaded) dots on the SIR-2000 screen. As each scan is collected by the system the screen fills with vertical, colored lines to generate a profile image of the subsurface.

  The Linescan color display is the best display for most applications, especially good for identifying buried point targets (ex. drums, voids, pipes). The Linescan grayscale display is a good display to identify buried pipes. The Linescan color or gray shade displays are also good for displaying geologic layering. You should try different Linescan color and grayscale displays of the same data sets to determine which displays help you best with the interpretation.

- Wiggle displays are sometimes better for interpreting layering in stratigraphic or geological surveys over long distances.

- Oscilloscope display allows viewing of a single radar trace in detail.

Linescan Display Parameters

Color Table: This parameter sets the Color (or gray scale) Table to be used to display the data. There are 15 possible Color Tables from which to choose. The Enter key is used to change the Color Table by toggling through the choices. The active Color Table is shown in the upper right hand corner of the SIR-2000 screen, above the oscilloscope display.

Each Color Table consists of 16 colors, eight colors to represent positive amplitudes and eight colors to represent negative amplitudes. Each data point in a scan is represented by a color or gray shade depending upon its value.

For example, using Color Table 2 low amplitude data values will show as black, high positive amplitudes as white and high negative amplitudes as gray. Thus, each scan results in a vertical line of colored (or gray shaded) dots on the SIR-2000 screen. As each scan is collected by the system, the screen fills with vertical colored (or grayscale) lines to generate a profile image of the subsurface.

The Linescan color display is a good display for most applications, but it is especially good to identify buried point targets (ex. drums, voids, pipes). The Linescan grayscale display is a good display to identify buried pipes.

Color Xform: This parameter sets the Color Xform (i.e., Transform) to be used to display the data. There are 8 possible Color Transforms from which to choose. The Enter key is used to change the transform. The active Color Transform is shown in the upper right hand corner of the SIR-2000 screen.

The Color Transform determines whether the color scale applied to the radar signal's amplitude is linear, logarithmic, or exponential. This function can also be used to de-emphasize certain features. For example, in a logarithmic display, all low amplitude signals are assigned into a "compressed" lower color range, and the range of high amplitude signals is extended. If white represents a high amplitude signal, then there will be more white area for a given data set than a linear transform. Transforms 2 and 3 are used to emphasize weak reflections, and Transforms 4 and 5 are used to emphasize high amplitude reflections.

During system setup you should always use Color Xform 1**, which is linear**. Though not required, we recommend using Color Xform 1 when collecting data.

During data playback Color Xform 2 is useful when viewing low amplitude regions and Color Xform 4 is useful when the objective is high amplitude targets (i.e., metal, or voids).

Vert Scale: This parameter controls the Vertical Scale labeling. The Vertical Scale can be set to Time, Depth Or None.

- If None is selected, no vertical scale will be printed.
- If set to Time**,** the vertical scale will be two-way travel time in nanoseconds.
- If set to Depth**,** the vertical scale will be in meters below the surface. Note that the depth scale is only approximate, and is based on an assumed dielectric constant of the subsurface for a single layer model. See the Diel parameter help for details. Note that the default Diel value is 1.

Diel: This parameter is the value of the dielectric constant used to convert two-way travel time to depth. The value ranges from 1 to 81 and depends upon the dielectric properties of the subsurface materials being profiled.

Approximate dielectric constants for various materials follow:

Material	Dielectric Constant	Material	Dielectric Constant
Air	1	Wet Sandstone	6
Snow Firn	1.5	Wet Granite	6.5
Dry Loamy/Clayey Soils	2.5	Travertine	8
Dry Clay	4	Wet Limestone	8
Dry Sands	4	Wet Basalt	8.5
Ice	4	Tills	11
Coal	4.5	Wet Concrete	12.5
Asphalt	5	Volcanic Ash	13
Dry Granite	5	Wet Sands	15
Frozen Sand & Gravel	5	Wet Sandy Soils	23.5
Dry Concrete	5.5	Dry Bauxite	25
Dry Limestone	5.5	Saturated Sands	25
Dry Sand & Gravel	5.5	Wet Clay	27
Potash Ore	5.5	Peats	61.5
Dry Mineral/Sandy Soils	6	Organic Soils	64
Dry Salt	6	Sea Water	81
Frozen Soil/Permafrost	6	Water	81
Syenite Porphyry	6		

Warning: Dielectric constants for various materials, and thus the resulting depth scales, are only approximations. For a description of methods for estimating the dielectric constant of the subsurface at your site, see your training notes.

Wiggle And O-Scope Display Parameters

Scale: The scaling parameter defines the number of vertical lines used to represent each wiggle. The larger the scale value, the larger the wiggle representation.

In O-Scope Mode, the scaling parameter defines the section of the amplitude scale observed.

- When Scale is 1, the full amplitude scale is shown.
- When Scale is 2, only the bottom 50% of the amplitude scale is shown.
- When Scale is 3, only the bottom 30% of the amplitude scale is shown, etc.
- Increasing the Scale parameter allows one to progressively zoom in on the scan.

Hor Scale: This parameter controls the Horizontal Scale labeling when in O-Scope Display Mode. The Horizontal Scale can be set to Time, Depth or None.

- If None**,** no horizontal scale will be printed in the Wiggle Mode, but a time scale will be printed in O-Scope Mode.
- If set to Time**,** the horizontal scale will be two-way travel time in nanoseconds.
- If set to Depth**,** the horizontal scale will be in meters below the surface.

Note that the depth scale is only approximate, based on the ASSUMED dielectric constant of the subsurface. See the DIEL parameter help for details.

Space: The spacing parameter sets how many vertical lines to move before printing the next wiggle. The higher the spacing value, the larger the spacing between wiggles.

Stack: The stacking refers to the number of incoming scans to stack for printing and display. This stacking does not apply to the recorded data. For example, a stack=4 will stack incoming scans into one (1) output scan for printing and display.

Skip: Skip refers to the number of scans to skip for printing and display. This will have no effect on the scans recorded. For example, a skip=1 will skip every other scan for printing and display. A skip of 2 will print a scan, skip two scans and print the next scan.

Saving The System Parameter Settings For Future Use

After setting up the system operating parameters, you may wish to save the setting for future use. This is done by using the Save Setup command accessed from the Setup command in the Collect Setup Menu block or the Playback Setup Menu block. This command is at the bottom of the second column of commands.

Save Setup

This command allows you to save all of the current system settings into a setup file. This file can then be recalled any time in the future and the system will be set to the current settings. Settings files can be recalled at any time using the Recall Setup command.

1. When this command is highlighted and the Enter key pressed, a list of 56 possible setup files will be displayed on the screen.
2. Use the Arrow keys to highlight the setup number where you wish to save the current settings.
3. Press the Enter key to save the settings.

Show Setup

This command shows the current system settings.

Chapter 4: Data Collection

Preparing For Data Collection

After setting the operating system parameters, either automatically or manually, you are ready to collect data. As a reminder, we have listed below three critical parameters that you should verify:

- Is the Disk Output set to ON?
- Have you selected the correct Run Mode, either Cont (continuous), SW (survey wheel) or Point (point collection)? If you are using a survey wheel, has it been calibrated?
- If you are going to print data real-time, have you selected the correct printer and set Print to ON?

The Collect Data Menu block is entered by pressing the Run/Standby key. What you see on the screen will depend upon the Run Mode you set.

- If the Run Mode is set to Cont (continuous), the system will begin collecting data and it will show across the screen. The file and scan number will appear in the lower right corner of the screen. A sign looking like [D] will appear at the bottom center of the screen if disk output is ON.
- If the Run Mode is set to SW (survey wheel), a scan will appear on the left end of the screen and the rest of the screen will remain blank until you begin to move the antenna/survey wheel.
- If the Run Mode is set to Point (point collection), a scan will appear on the left end of the screen. The rest of the screen will remain blank until you press the Run/Standby key or the marker to begin collect the next data point or survey station.

Continuous Data Collection Method

The antenna is pulled continuously across the ground and the SIR-2000 collects data at the number of scans per second selected. The data collection rate is independent of the speed at which the antenna is pulled. The resulting subsurface profile is referenced to a ground location via the operator placing electronic marker events on the data as the antenna crosses survey grid points.

1. Start collecting data by pressing the Run/Standby key or a marker switch connected to your antenna once.
   - Each subsequent pressing of the switch will place a mark in the radar record.
   - Pressing the Up Arrow key on the control unit will also generate marks.
2. To stop collecting data at the end of a survey line press the Run/Standby key. The system will now be in standby mode and the data for that line can be reviewed.

3. To stop collecting data, close the data file and start another line, press the Run/Standby key and **HOLD IT DOWN FOR 2 SECONDS**.
   - Note that this method of closing the file can only be done when the system is collecting data.
   - If the system is in Standby, you must first press Run/Standby to begin collection, then press Run/Standby and hold it down for 2 seconds.
   - A file may also be closed while in Standby if the *Enter* key is pressed (to bring up menu), then select Go To Setup.
   - To stop collecting data from the antenna marker, press and hold the Marker button for 2 seconds to close the data file. The system is now ready to begin collecting the next data file.

When the Run/Standby key is pressed to begin data collection, the speaker will emit a single BEEP. When a data file is closed, the speaker will emit a double BEEP.

Reviewing The Current Data File By Scrolling: If the current data file is greater than one screen, the data file (up to the limit of the system memory) can be reviewed using the SIR-2000 scroll capability.

1. Press the Run/Standby key to put the system in Standby.
2. Use the Right arrow key to view data to the left of the current data screen and use the Left arrow to view data to the right of the current data screen.

The Collect Data Menu Commands

This menu must be accessed after data collection has begun. During data collection, press Run/Standby to enter Standby, then press Enter to bring up the menu.

Collect: Selecting this command will start the system collecting data. The output device, either a Disk File number or RAM will be shown in the bottom right hand corner of the screen as the data is collected.

Cursor: When Cursor is activated, dashed cross-hairs appear on the screen. The horizontal line gives the time-depth of an object in nanoseconds (ns) if the Vert Scale Display parameter is set to time. If the Vert Scale Display parameter is set to Depth, the horizontal line gives the depth of an object in meters.

2D Grid: This function is not operational at this time.**Line:** When 2d Grid is operational, this parameter is the line number that will be entered into the file header for the next line of data to be acquired.

StartP: When 2d Grid is operational, this parameter is the Y coordinate value for the starting point of the line.

EndP: When 2d Grid is operational, this parameter is the Y coordinate for the ending point of the line.

Mark Intvl: When 2d Grid is operational, this parameter is the Y coordinate interval between marker (survey grid) locations along the line.

Step: For the parameter shown in the box above, this is the increment that will be used when changing the value of the parameter.

After the desired value of the parameter is set, press the Enter key to register that value in the system.

Select Block: This command is used to select a block of data for printing or saving to disk. The block of data selected can be more than one screen size.

1. When this command is selected, the command menu will disappear from the screen and a vertical line (cursor) will appear in the middle of the screen.
2. Move the cursor using the Right and Left arrow keys until it is on the first (leftmost) scan of the block of data you want to select.
3. Press the Down arrow key to select the beginning of the block.
4. Now, using the Right arrow key, move the cursor until it is on the last (furthest to the right) scan of the block of data you wish to select.
5. As you move the cursor, a crosshatched diagonal highlighted area will appear over the data that will be selected. Press the Up arrow key to complete the selection.
6. Press the Print key to print the selected data block.
7. Press Enter and then select Dump To File to save the selected block in a file.
    - If Disk On is selected, data will be stored to the file with name FILENAME+L (a letter A-Z will be appended to the original file name), otherwise a file name with a number greater than the last file number recorded will be created.
8. Press the Enter key to exit the Select Block function.

Dump To File: This command enables you to save a selected block to a separate data file. After a block of data has been selected, highlight the Dump To File command and press Enter.

Drop Menu: This command will cause the command menu to disappear, so the bottom of the data can be viewed.

Go To Setup: Selecting this command will put the system in the Collect Setup Mode, and close the current file.

Survey Wheel Controlled Data Collection Method

In this mode of operation a survey wheel attached to an antenna controls the scanning of the SIR-2000 system. Parameters are set so that data are acquired at fixed intervals. *This is the most accurate survey method.*

1. Start collecting data by pressing the Run/Standby key or a marker connected to your antenna.

2. Start pulling the antenna along the survey line and data will begin to appear on the screen. If you stop pulling the antenna data will stop being collected. DO NOT BACK UP the antenna because this will cause your survey distance to be incorrect.
3. Continue pulling the antenna until the end of the survey line.
4. To stop collecting data at the end of a survey line press the Run/Standby key. The system will now be in standby mode and the data for that line can be reviewed.
5. To close the data file and start another line press the Run/Standby key and hold it down for 2 seconds.
6. To stop collecting data from the antenna marker, press and hold the Marker button for 2 seconds and close the data file. The system is now ready to collect the next file.

***Note*:** If the system speaker sounds a continuous BEEPing sound while collecting data with a survey wheel, you are pulling the antenna too fast. Either slow down your rate of acquisition, decrease the Scans/Unit value in the survey wheel setup, or increase the scan rate in Collect Data Setup.

Discrete Data Point Data Collection Method

There are certain field situations where the continuous mode data collecting method is not practical, and it is only possible to collect data with the point-by-point method. Two such situations are: data collection in mines where the walls are not flat, and in heavily overgrown field sites such as many landfills. Also, in cases where deep penetration is necessary, or in conductive subsurface conditions, it is sometimes advantageous to use the discrete data point collection method with large stacking values.

1. Start collecting data by pressing the Run/Standby key or a marker connected to your antenna. The system will output one scan and then standby.
2. Move the antenna to the next station and press the Run/Standby key or the antenna marker key to collect a scan at that station.
3. Continue this collection technique until the end of the survey line.
4. To stop collecting data at the end of a survey line press the Run/Standby key and hold for 2 seconds at the last station. This will close the file and the system will be ready for the next survey line.

***Note*:** The antenna marker switch cannot be used to close the data file at the end of a line in point mode. You must use the *Run/Standby* key to close the file in this mode. This is done by holding the *Run/Standby* key depressed for 2 seconds at the last station on the line.

Chapter 5: Data Playback And Review

Selection of files to playback and setup of system display, processing and output during playback are done in the Playback Setup Menu block. Playback of data already collected and stored on the disk is done via the Playback Data Menu block.

Playback Setup Menu Block

This block is entered when the system is powered ON without an antenna, or from the Playback Data Menu block by entering the Setup command. It is entered from the Collect Setup Menu block by pressing the Collect/Playback key.

Setup For Processing Of Playback Data

During playback, Gains, Horizontal Filters and Vertical Filters can be applied to the data to improve interpretation.

Setup: When this command is highlighted, a set of playback processing parameters that can be set appears in the second column. The commands that will appear in the second column are; Processing, Play All, Save Setup, Recall Setup, and Show Setup.

Pressing the Enter key when Setup is highlighted will have no effect.

When Processing is highlighted, the following options appear in a menu box to the right:

- **Gain:** This function is used to apply an additional gain constant to the data files as they are played back to the system or transferred to a computer. You can apply this gain if the data acquired is too low in amplitude and difficult to interpret.

  Activating this function will cause a parameter setup box to appear to the right. Use this box to adjust the value of the gain to be applied.

  When setting the values of the gain, the Up arrow is used to increase the value of the parameter and the Down arrow is used to decrease the value of the parameter.

  The Right and Left arrows are used to increase or decrease the increment when setting the gain values. The gain values are in units of decibels (dB). Every 6 decibel increase is equivalent to doubling the amplitude of all points in the signal.

***Caution*:** Gains applied to the data during playback are not stored in the data file. They are only applied to the displayed data. When gains are applied to the data during playback and data transfer is ON, or DISK=ON, the data stored on the receiving computer or the internal hard disk will have this additional gain applied. The internal hard disk file will have a letter appended to the original file name.

- **Filters:** When this command is highlighted, a series of data filter commands will appear in the third column. The filters are: Vert HP (vertical high pass), Vert LP (vertical low pass), Hor Smooth (horizontal smoothing), and Hor Bkgr Rm (horizontal background removal). These filters are used to improve signal clarity.

  - The Vert HP (high pass) filter is used to eliminate low frequency noise (i.e. signal drift).

- The Vert LP (low pass) filter is used to remove high frequency noise ("snow").
- The Hor Smooth (horizontal smoothing) filter is used to horizontally smooth the data (enhances layers).
- The Hor Bkgr Rm (horizontal background removal) is used to improve the recognition of small targets by removing horizontal bands produced by noise, reverberations or flat reflecting layers.
- The units of the vertical filters are in MHz and the horizontal filters are numbers of scans.

- **Clr Proc:** When this command is highlighted and activated by pressing the Enter ↵ key, any data playback processing set (i.e., Gain and Filters) will be reset to zero and turned off. There will be no additional data processing during playback.
- **Play All:** When this command is selected, all data files stored on the hard drive will be played back to the display and printed, if a printer is connected to the SIR-2000 and turned ON. This option allows the user to print all the files while the system is unattended.
- **Save Setup:** This command allows you to save the current playback setup in a file you designate (SETUP_1 to SETUP_56) for future use.
- **Recall Setup:** Allows you to recall previously saved system setups.
- **Show Setup:** Displays the current system setup parameters.

Data Display And Printing During Playback

There are three types of displays available during playback, Linescan, Wiggle and O-Scope. These displays can be printed during playback on the T-104, DPU-5400 (Seiko Model DPU5400 4" thermal plotter) or the GS-608P (OYO Model GS-608P 8" thermal plotter).

Output: When this command is highlighted, the output setup commands appear in the second column. Pressing the Enter ↵ key when Output is highlighted will have no effect.

Print: This function turns the print output ON or OFF by pressing the Enter ↵ key. When it is turned ON, a third column of printer control commands appears.

Disk: Disk ON writes the playback file to the hard drive and appends a letter to the filename each time the file is saved.

XFER: See the Section Transferring Data from the SIR-2000 to a Computer in Chapter 7.

Printer: Use this command to select the printer you will be using to print the data. The Enter ↵ key is used to toggle between the supported printers. Make sure the printer cable is connected and the printer turned ON before selecting the printer.

The maximum real-time scan rate when printing is 32 scans/sec.

Horizontal Zoom: This parameter stretches the data printout in the horizontal direction. The possible values are 1, 2, 3, or 4 and the Enter ↵ key is used to change the value.

A value of 1 means that each scan of a data file is printed as one scan on the printer. A value of 2 means that each scan of a file is output as 2 duplicate scans on the printer. A value of 3 means

that each scan of file is output as 3 scans on the printer and a value of 4 means 4 scans are printed for each scan in a data file.

When in Linescan Mode the T-104 and the GS-608P print 203 scans per inch. The SIR-2000 video display displays 94 scans per inch. The Horizontal Zoom setting of 2 will give the best match between the aspect ratio of the video screen and that of the printout.

Orientation: This parameter controls the orientation of the data as it is printed on the paper. The orientation can be Normal or Flipped and is changed by pressing the Enter ↵ key.

In the Normal setting, the top of the data will print at the top of the paper. In the Flipped setting, the top of the data will print at the bottom of the paper.

This feature is useful when adjacent survey lines are collected in opposite directions. When the direction of data collection is reversed and the data printout is set to Flipped**,** you will be able to align all the printouts and compare adjacent features. For example, if the odd-numbered survey lines (1,3,5,7...) are collected from East to West and printed Normal, and the even-numbered survey lines (2,4,6,8...) are collected from West to East and printed Flipped, you will be able to align all printouts in their proper perspective and compare features.

Display: This command controls how the data is displayed on the video screen and printer. There are three types of data display; Linescan, Wiggle, and O-Scope. Use the Enter ↵ key to toggle through the three types of displays. When the display type is changed, the appropriate Display parameter menus requiring input appear in the column three.

Color Table: This parameter is only used when Display=Linescan.

This parameter sets the color (or gray scale) table to be used to display the data. There are 15 possible Color Tables from which to choose. The Enter ↵ key is used to toggle through the color table choices. The active Color Table is shown in the upper right hand corner of the SIR-2000 screen.

Each color table consists of 16 color bins, eight colors to represent increasing positive amplitudes and eight colors to represent increasing negative amplitudes. Each data point in a scan, depending upon its amplitude value, is represented by a color or gray scale. For example, using Color Table 2, low data amplitudes will show as black, high positive amplitudes as white and high negative amplitudes as gray. Thus, each scan results in a vertical line of colored (or gray shaded) dots on the SIR-2000 screen. As each scan is collected by the system, the screen fills with vertical colored (or grayscale) lines to generate an image profile of the subsurface.

The Linescan Color display is the best for most applications, and especially good to identify buried point targets (ex. drums, voids, pipes). The Linescan Grayscale display is good to identify buried pipes.

Color Xform: This parameter only used when Display=Linescan**.**

This parameter sets the Color Xform (i.e., Transform) to be when displaying data. There are 8 possible Color Transforms from which to choose. The Enter ↵ key is used to change the transform. The active Color Transform is shown in the upper right hand corner of the SIR-2000 screen.

Different Color Transforms will emphasize different amplitude aspects of the data. Compare Color Xform 3, which emphasizes the low data amplitudes and will represent the data with multiple colors, with Color Xform 5, which emphasizes the high data amplitudes and will decrease the amount of color representing the data.

During system setup you should always use Color Xform 1 (linear). We also recommend using Color Xform 1 when collecting data.

During data playback Color Xform 2 is useful when viewing low amplitude regions and Color Xform 4 is useful when the objective is to see only high amplitude targets (i.e., metal, or voids).

Vert Scale: This parameter controls the vertical scale labeling. The vertical scale can be set to Time, Depth or None. If None is selected, no vertical scale will be printed. If set to Time, the vertical scale will show two-way travel time in nanoseconds.

If set to Depth, the vertical scale will display meters below the surface. Note that the depth scale is only approximate, and based on an *assumed* dielectric constant value for the subsurface. See the Diel parameter help for details.

Diel: This parameter is the value of dielectric constant used to convert two-way travel time to depth. The value can range from 1 to 81 or more and varies greatly with electrical and physical properties of the subsurface materials. Note: The default dielectric value for a depth scale is 1. Be sure to select an appropriate dielectric value before collecting/playing back data.

Approximate dielectric constants for various common materials follow:

Material	Dielectric Constant	Material	Dielectric Constant
Air	1	Wet Granite	6.5
Snow Firn	1.5	Travertine	8
Dry Loamy/Clayey Soils	2.5	Wet Limestone	8
Dry Clay	4	Wet Basalt	8.5
Dry Sands	4	Tills	11
Ice	4	Wet Concrete	12.5
Coal	4.5	Volcanic Ash	13
Asphalt	5	Wet Sands	15
Dry Granite	5	Wet Sandy Soils	23.5
Frozen Sand & Gravel	5	Dry Bauxite	25
Dry Concrete	5.5	Saturated Sands	25
Dry Limestone	5.5	Wet Clay	27
Dry Sand & Gravel	5.5	Peats	61.5
Potash Ore	5.5	Organic Soils	64
Dry Mineral/Sandy Soils	6	Sea Water	81
Dry Salt	6	Water	81
Frozen Soil/Permafrost	6		
Syenite Porphyry	6		
Wet Sandstone	6		

Warning: Dielectric constant values for various materials and the resulting depth scales are only approximations. For a description of methods for estimating the dielectric constant of the subsurface at your site, see your training notes.

Wiggle And O-Scope Display Parameters

The scaling parameter defines the number of vertical lines used to represent the amplitude of each wiggle. The larger the scale value, the larger the wiggle representation.

In O-Scope Mode, the scaling parameter defines the section of the amplitude scale observed. When Scale is set to 1, the full amplitude scale is shown. When Scale = 2, only the bottom 50% of the amplitude scale is shown. When Scale = 3, only the bottom 30% of the amplitude scale is shown, etc.. Increasing the Scale parameter allows one to progressively zoom in on the scan.

Hor Scale: This parameter controls the horizontal scale labeling when in O-Scope Display mode. The horizontal scale can be set to Time, Depth or None.

- If None is selected, no horizontal scale will be printed in wiggle display, time lines will be printed in O-Scope display.
- If set to Time, the horizontal scale will be two-way travel time in nanoseconds.
- If set to Depth, the horizontal scale will be in meters below the surface.

Note that the depth scale is only approximate, based on the assumed dielectric constant of the subsurface. See the Diel parameter help for details.

Space: The spacing parameter determines how many vertical line spaces to skip before printing the next wiggle. The higher the spacing value, the larger the spacing between wiggles. This function will have the effect of lengthening a radar profile.

Stack: Stacking refers to the number of incoming scans to stack (add) for print and display purposes only. Stacking does not apply to the recorded data. For example, setting Stack = 4 will stack 4 incoming scans into one (1) output scan for printing and display. This function will have the effect of shortening a radar profile.

Skip: Skip refers to the number of scans to skip for print or display purposes only. This will have no effect on recorded data. For example, a Skip = 1 will skip every other scan for printing and display. A Skip of 2 will print (display) a scan, skip two scans and print (display) the next scan. This function will have the effect of shortening a radar profile.

Selecting Files For Playback

Activate the Files command and then choose Select or Select All (the Select All command is at the bottom of the second column) from the second column.

- The Select command allows you to choose individual files or groups of files to playback. This is accomplished by highlighting the file or files you want to playback with the cursor, and then pressing the Enter ↵ key.
- This action will place a box around the file(s) you have selected, and the SIR-2000 will play them back when the Run/Standby is pressed.

- The first time the Run/Standby key is pressed, the file header will be displayed.
- The second time the Run/Standby key is pressed, the file will play back. If the file is longer than one screen, you can scroll back and forth through the file using the Right and Left arrow keys.
- The Select All command will select all files on the disk for playback.

Playback Data Menu Block

This block is entered from the Collect Data Menu block by pressing the Collect/ Playback key. It is entered from the Playback Setup Menu block by pressing the Run/Standby key.

Reviewing The Current Data File By Scrolling

If the current data file size is greater than one screen, the data file (up to the limit of system memory) can be reviewed using the SIR-2000 scroll capability.

1. Press the Run/Standby key to put the system in Standby.
2. Use the Right arrow key to view data to the left of the current data screen and use the Left arrow to view data to the right of the current data screen.

The Playback Data Menu Commands

Playback: This toggle command will alternatively display the current file header on the screen or clear the data section of the screen.

Cursor: When Cursor is activated, a dashed crosshairs appears on the screen. The horizontal line gives the two-way travel time from the beginning of the scan to the object in nanoseconds (ns) if the Vert Scale display parameter is set to Time. If the Vert Scale display parameter is set to Depth, the horizontal line gives the depth of an object in meters.

***Caution*:** The measurement of two-way travel time or depth assumes that the surface reflection is at the top of the data screen. If it is not then the measurements will be incorrect.

View: This function controls the data viewing on the screen. It has four settings; Full, Upper, Middle, and Deep. It does not affect the recorded data. Use the Enter key to toggle through the views.

- The Full view displays the full data scan on the screen.
- The Upper view displays the upper third of the data on the full screen. It is a zoom view on the shallow data.
- The Middle view displays the middle third of the data on the full screen. It is a zoom view on the middle section of data.
- The Deep view displays the bottom third of the data on the full screen. It is a zoom view on the bottom third of data.

For example: If a range of 120ns was set, the Full view would display 0-120ns, the Upper view would display 0-40ns, the Middle view would display 40-80ns and the Deep view would display 80-120ns. Note that the cursor coordinates refer to the last view selected. For example, if the first

half of the screen is the full view and the last half is the deep view, the cursor will assume the range for the deep view over the entire screen.

Select: This command is used to select or deselect files to be played back by the system for review. When this command is activated, a list of data files will appear on the upper portion of the screen. Use the Arrow ← ↑ ↓ → keys and the Enter ↵ key to select the files that you wish to playback for review.

Select Block: This command is used to select a block of data for printing or saving to disk. The block of data selected can be more than one screen size. When this command is selected, the command menu will disappear from the screen and a vertical line (cursor) will appear in the middle of the screen.

1. Move the cursor using the Right → and Left ← arrow keys until it is on the first (left-most) scan of the block of data you want to print.
2. Press the Down ↓ arrow key to select the beginning of the block.
3. Now using the Right → arrow key, move the cursor until it is on the last (right-most) scan of the block of data you wish to print. As you move the cursor, a crosshatched diagonal highlight box will appear over the data that you select.
4. Press the *Up* ↑ arrow key to input the end of the block you are interested in.
5. Press the Print key to print the selected data block, or use the Dump To File command to save the selected block into its own file.
    - If Disk On is selected, data will be stored to the file with name FILENAME+L (a letter A-Z will be appended to the original file name), otherwise a new file name with one higher number than the last file name will be created.
6. Press the Enter ↵ key to exit the Select Block function.

Dump To File: This command enables you to save a selected block to a separate data file. After a block of data has been selected, highlight the Dump To File command and press Enter ↵.

Drop Menu: This command will cause the command menu to disappear, allowing the bottom of the data to be viewed.

Go To Setup: When the system is in the Collect Data Mode, selecting this command will put the system in the collect setup mode. When the system is in the Playback Data Mode, selecting this command will put the system in the Playback Setup Mode.

Chapter 6: Operation With The GSSI Thermal Plotters

Three thermal printers the T-104, the DPU-5400 and the GS-608P can be used with the SIR-2000 control unit to provide field prints of your data. Data can be printed either in real-time (i.e., during acquisition) or during playback from disk.

***Note*:** Because of the high data acquisition rate of the SIR-2000, only the GSSI T-104, DPU-5400 and GS-608P printers can be used with the SIR-2000. Other printers are not supported.

After turning on the SIR-2000, connect one end of the SIR-2000 printer cable to the parallel connector of the SIR-2000 and the other end to the printer. The connector is on the underside of the DPU-5400 and on the topside of the GS-608P. Turn the printer ON.

1. From the Collect Setup Menu block, select Output and then turn Print to ON.
2. Select the Printer type.
3. Set the Horizontal Zoom to 1 if printing during data collection. The Horizontal Zoom can be set to other values if printing during data playback.
4. Set the Orientation to Normal.
5. Enter the Collect Data or Playback Data Menu blocks and collect or playback data. The data will now be printed.

***Note*:** The printer should not be connected during power-up of the SIR-2000. If the SIR-2000 seems to hang-up during the power-up sequence, disconnect the printer (or parallel data transfer) cable.

Chapter 7: File Operations - Compress, Delete & Transfer

In order to keep the SIR-2000 disk working efficiently during data collection, it is important to effectively manage the disk files. Data file compression, decompression, deletion, and transfer to a computer are accessed from the Files command in the first column of the Playback Setup Menu block or the Collect Setup Menu block.

***Note*:** If you wish to compress, delete or transfer all the disk files, or a majority of the files, you should first activate the Select All command at the bottom of the second column of the File commands.

File Compression To Save Disk Space

Compression commands are accessed from the Files command in the first column of the Playback Setup Menu block or the Collect Setup Menu block.

Compress: Compress data files to save room on the data storage disk or to make them smaller for data transfer. When the highlight bar is moved to this command, two compression commands appear in the third column, Method and Do Compress.

- **Method:** There are four possible compression methods, 16-8 (16 bit data resample to 8 bit data), Resamp (saves every other data sample), Rescan (saves every other data scan) and Stat (variable 4-16 bit resample). The 16 to 8 resampling will compress 16 bit files by about 50% , but it will not compress 8 bit data files. The other methods will compress all data files by approximately 50% or more. After a file is compressed, you cannot recover the original file unless you choose to save it during the compression.

  Rescan and Resamp compression take approximately 1 minute per megabyte of data. The 16-8 compression takes approximately 45 seconds per megabyte of data.

- **Do Compress:** When this command is activated, the directory of stored data files appears on the screen. Select the files you wish to compress, or all files, and then begin the compression. You will be asked if you want to store the original data files. If the answer is YES, the original files are saved under the original name and the new files are saved as FILENAME+_0 or FILENAME+0 (a _0 or 0 is added to the original file name). If more than one compression is done, -1, -2, -3... will be appended to the file name rather than -0.

Deleting Data Files To Save Disk Space

The Delete command is accessed from the Files command in the first column of the Playback Setup Menu block or the Collect Setup Menu block

Delete: When this command is activated, the directory of stored data files appears on the screen. Select the files you wish to delete and then begin the deletion process by pressing the Run/Standby key. You will be asked to confirm deletions.

Transferring Data Files From The SIR-2000 To A Computer

Data Transfer via Parallel Port

To transfer data to a computer, you must first connect the SIR-2000 parallel data transfer cable from the SIR-2000 PARALLEL connector to an enhanced **bi-directional** parallel port (EPP) in the computer. Both the computer and sir-2000 must be turned on before connecting the parallel data transfer cable. Simple to install, bi-directional parallel port computer cards are available from GSSI.

***Warning*:** The SIR-2000 parallel data transfer cable should only be connected to an enhanced bi-directional parallel port (EPP) in your computer. The parallel ports of most computers are output only. If you connect the parallel data transfer cable to an output only parallel port on your computer, damage will occur to the computer parallel port. If you are uncertain that your computer has a bi-directional parallel port, do not connect the cable and try it. Refer to your computer manual or call your computer sales representative. GSSI is not responsible for any damage that occurs to computer parallel ports.

Simple to install, enhanced bi-directional parallel port (EPP) computer cards are available from GSSI. Or, when ordering a new computer, request that the manufacturer install a bi-directional parallel port. The extra cost is normally very low.

Step 1: First, configure the software on the receiving computer. We recommend using Data Transfer Utility for Windows available free of charge from www.geophysical.com. S*ee Appendix D for the detailed instructions on its installation and use*.

Alternatively, the DOS-based SIR2FTR can be used for data transfer.

Step 2: Copy SIR2FTR.EXE from the Utility disk supplied with your system, to the directory on your computer where you want to store the transferred data files. Start the transfer program on your computer by typing:

SIR2FTR PP:(address of the parallel port)

If you purchased a bi-directional parallel port card from GSSI the above command would be: SIR2FTR PP:278

where 278 is the address of the parallel port. If your computer has already installed a bi-directional parallel port, you must enter the correct address. To determine the address of your bi-directional parallel port, refer to your computer documentation.

Transfer: The file transfer command (Transfer**)** is accessed from the Files command in the Collect Setup Menu block or the Playback Setup Menu block.

When the SIR-2000 Transfer command is activated, a directory of the data files stored on the SIR-2000 appears on the screen. Select the files you wish to transfer and then begin the transfer process. Data is transferred at a rate of approximately 30 kilobytes/second.

Alternate Transfer Method: Applying Gains & Filters

During data playback on the SIR-2000, additional filters and gains can be applied to the and the processed data can be transferred to a computer. If, during the data playback process, you wish to

simultaneously transfer data to a computer, set XFER command from the Playback Setup Output Menu to ON. Go to the Playback Data Menu block and use the normal procedure to playback files. As the data is played back, it will be transferred to the computer. The transferred data files will contain any playback processing applied.

Data Transfer via Serial Port

Serial data transfer is also possible, though not recommended because of slow speed and complicated procedure. If for some reason you're unable to transfer data via parallel port, contact GSSI for serial transfer instructions.

Chapter 8: System Operations

Setting The System Date & Time Clock To Your Local Time

The system maintains the current date and time and this information is entered in the file headers as the data is collected. It is important that the date and time are accurate. Time and Date are accessed from the System command in the first column of the Collect Setup Menu block or Playback Setup Menu block.

When Clock Set is selected via the Enter ↵ key, the current system time and date appear on the screen with an instruction block describing how to change the time and date.

Procedure To Upgrade The Operating System Software

The following procedure should be used to update or upgrade you SIR-2000 operating system when you receive an update or upgrade from GSSI. Your computer must be operating under MS-DOS v6.2, or higher, to perform the upgrade.

You will be using the standard MS-DOS v6.2 functions, INTERLNK and INTERSVR, to upgrade. **Should you have any trouble with this procedure, please refer to your MS-DOS manuals included with your system**.

1. Turn on your SIR-2000 and the computer you will be using for the upgrade. Your computer must be operating under MS-DOS v6.2 to perform the upgrade. If your computer has not been upgraded to MS-DOS v6.2 yet, you can install the licensed copy of MS-DOS v6.2 provided with your SIR-2000.
   - Change the config.sys file on your computer to include the line

     device=C:\dos\interlnk.exe

   Save the new config.sys file and reboot your computer. Your computer's config.sys file has now been changed to include the interlnk command.
2. Connect a null modem cable between the COM1 serial port of your computer and the serial connector of the SIR-2000 system.
3. Connect a keyboard to the keyboard connector of the SIR-2000.
4. Enter the Collect Setup Menu of the SIR-2000.
5. Press the <*ALT*><*S*> keys on the keyboard connected to the SIR-2000. The SIR-2000 will exit the operating system and the prompt: **C:>** will appear.
6. Type: **intersvr** on the SIR-2000. The interserver menu will now appear.
7. On the computer enter the upper level directory by typing: **CD **
8. Start the interlnk program on your computer by typing: **interlnk**

9. On the SIR-2000 screen are listed the drives of the computer and the SIR-2000. This screen will tell you which drive on the SIR-2000 equals the C: drive on the computer. Use this SIR-2000 drive letter in the next few commands. In the instructions below, we assume that the E: drive on the SIR-2000 equals the C: drive on the computer.

   On the computer, make a new directory by typing: **mkdir** (sir2 drive letter)**:\sir2up**

   For our specific example we would type: mkdir E:\sir2up

10. Insert your SIR-2000 upgrade disk into the floppy drive of your computer and copy the files from the upgrade disk to the SIR-2000 by typing:

    Copy (computer floppy drive letter)**:*.* E:\sir2up*.***

11. After the files have finished copying, the DOS prompt will reappear on the computer.
12. Press *<Alt>* *<F4>* H$ on the keyboard attached to your SIR-2000 to exit the intersvr program.
13. Enter the sir2up directory on the SIR-2000 by typing: **cd \sir2up**
14. Finish the upgrade on the SIR-2000 by typing: **upgrd**

    A few messages will appear on the SIR-2000 screen. You should see the following important ones:

    START OF LOAD

    (loading counter that increases as the program is loaded)

    END OF RUN

15. After the upgrade is complete delete all upgrade files in the SIR-2000 by typing: **Delete \sir2up*.***
16. Turn the SIR-2000 system OFF and then ON (re-boot). The upgrade is now complete.

Hard Disk Maintenance

After approximately every 40 hours of use, two software maintenance functions for the SIR-2000 data storage hard disk should be performed to locate lost clusters and disk defragmentation.

1. Connect a null modem cable to the serial port of the SIR-2000.
2. Connect a keyboard to the keyboard connector of the SIR-2000.
3. Enter the Collect Setup Menu of the SIR-2000.
4. Press the *<ALT><S>* Hs keys on the keyboard connected to the SIR-2000. The SIR-2000 will exit the operating system and the prompt: **C:>** will appear.
4. Change to the D: drive by typing: **D:**

5. To check for lost clusters, type the following command:

SCANDISK /AUTOFIX /NOSAVE /NOSUMMARY

and answer **Y**.

For details on the SCANDISK command at the DOS prompt type: **SHELP SCANDISK**

To exit HELP SCANDISK type: <*ALT*> <*F*><*X*> Hfx

6. Now defragment your hard disk by typing: **DEFRAG /B**

   Select C: drive to optimize.

7. After DEFRAG is complete, turn the system OFF and ON to return to the operating system.

Chapter 9: Automatic Operation

Data Collection

The Automatic Operation Mode is initiated by pressing the Run key when the SIR-2000 is first turned ON and you are given the option at the first menu screen. When this is done, the system will be in Data Collection Set-Up Mode, and you will see a menu on the left side of the screen, and an oscilloscope display of the reflected radar signal on the right.

- The Data Collection Menu group will be surrounded by a solid white line, indicating that it is active.
- The Playback Menu will be surrounded by a dashed white line, indicating that it is inactive. To activate Playback Mode, toggle the Collect/Playback key.

The Automatic Mode of operation was developed to allow simplified operation of the SIR-2000 system for the special application of pavement and bridge deck analysis. The menu is less complicated and allows input control over the following parameters; first by highlighting the menu option with the arrow keys, and then using the Enter key and the Arrow keys to input a value.

In the Data Collection Menu:

Range: 1 to 3 meters in half-meter steps

Gain: -10 to 10 dB

Dielectric: 0 to 99 - as this value is increased, the time scale on the oscilloscope display also increases, to a maximum of about 70ns.

Resistivity: 0 to 9999. If you do not know this value for the material you are scanning, set to zero.

Encoder: ON or OFF

Y-Axis: TIME or DEPTH

In the Output Menu:

Disk: ON or OFF

Display: COLOR or GRAY

Printer: ON or OFF

File Name: assigned by system when DISK is turned ON, otherwise RAM

Once you have chosen your operating parameters, you can put the system into data acquisition mode by pressing the Run/Standby key.

- If the disk is turned OFF, a courtesy check will appear asking you if you want to start data collection with the disk output OFF, and allows you to reply Cancel or OK.
- If you select OK, the system will start scanning, and the output will go to RAM.

The upper left side of the screen shows the linescan image of the radar profile being collected, the upper right shows an oscilloscope image of the reflected radar signal, and the bottom of the screen shows the current system parameters.

If your data file exceeds the memory limits of RAM (16 MB), the first part of the record will be written over by data currently being recorded.

- Pressing the Run/Standby key at this time will put the system into Standby and a cursor will appear in the radar profile. A scale listing scan numbers will also appear at the bottom of the radar image.
- You can navigate the cursor around the radar image using the Arrow keys, and the window labeled “cursor” will contain position and amplitude information of features you indicate with the cursor.
- If you get to either end of the image, the screen will display the next or previous 50 scans, depending on which direction you are going.
- Pressing the Run/Standby key again will return the system to Data Acquisition Mode.
- When in Data Acquisition Mode, pressing the Run/Standby key and holding it down for 2 seconds will stop the system scanning and close the file, and the system will return to Setup Mode.

Data Playback

Playback Mode is entered by toggling the Collect/Playback key. The Playback Menu will now be surrounded by a solid white line indicating it is active. In Playback Mode you have the following operational options, which you select and change by navigating through the menu the same way as in Collect Mode:

File Name: allows you to select the file you want to playback for review or printing.

Display: allows you to select from either color or grayscale.

Printer: ON or OFF

Print ZOOM: variable from 1 to 5. A value of 1 means that each scan of a data file is printed as one scan on the printer. A value of 2 means that each scan of a file is output as 2 duplicate scans on the printer. A value of 3 means that each scan of a file is output as 3 scans on the printer, etc.

When in Linescan Mode the T-104 and the GS-608P print 203 scans per inch. The SIR-2000 video display displays 94 scans per inch. A Horizontal Zoom setting of 2 will give the best match between the video screen and the printout.

- Once a file is selected, you can play it back by pressing the Run/Standby key.
- You can stop the system playing back at any point in the file by pressing Run/Standby again. This will pause the playback and allow you to move the cursor around to points of interest in the data.
- You can make position and signal amplitude measurements, which can help you in data interpretation.
- To resume playback, press the Run/Standby key again.
- When you reach the end of the file, the image will stop scrolling, and the cursor will appear superimposed on the data.
- To exit Playback Mode, and return to standby, toggle the Collect/Playback key.

Appendix A: Contents Of The Parameter Setup Files

Brief Description Of Pre-Loaded Setups

2500HS	This setup is for the 2500 MHz Horn antenna at high data acquisition speed. Maximum data acquisition speed 80kph (50mph) with a sample interval of 0.4m. Range 10ns.
2500HHR	2500 MHz Horn antennafor high horizontal resolution pavement evaluation. Maximum data acquisition speed 11kph (7mph) with a horizontal sample interval of every 1 cm. Range 10ns.
1500	1500 MHz antenna (5100) for automatic processing in RADAN NT (Bridge and Concrete modules). Range 10 ns
1500_2	1500 MHz antenna (5100) for visual inspection and manual processing. Range 12 ns.
1000HS	1000 MHz Horn Antenna at high data acquisition speed. Maximum data acquisition speed 80kph (50mph) with a sample interval of 0.4m. Range 20 ns.
1000HHR	1000 MHz Horn Antenna for high horizontal resolution road evaluation. Maximum data acquisition speed 11kph (7mph) with a horizontal sample interval of every 1 cm. Range 20ns.
1000TAD	1000 MHz standard antenna for concrete and roadway evaluation. Depth of viewing window is approximately 1m. Range 15ns.
1000TAS	1000 MHz standard antenna concrete and roadway evaluation. Depth of viewing window is approximately 50cm. Range 8ns.
900TAVD	900 MHz antenna shallow archeological and airport runway investigations. Depth of viewing window is approximately 2m. Range 30ns.
900TAD	900 MHz antenna concrete, roadway and runway evaluations. Depth of viewing window is approximately 1m. Range 15ns.
900TAS	900 MHz antenna concrete and roadway evaluations. Depth of viewing window is approximately 50cm. Range 8ns.
500D	500 MHz antenna “deep” viewing depth. Range 100ns.
500S	500 MHz antenna “shallow viewing depth. Range 60ns.
500DPH	500 MHz dual power antenna on high transmit power setting. Range 100ns.
500DPL	500 MHz dual power antenna on low transmit power setting. Range 100ns.
400D	400 MHz antenna, “deep” viewing depth. Range 100ns. Appropriate for utilities, archaeology surveys, etc.
400S	400 MHz antenna, “shallow viewing depth. Range set at 60ns. High resolution for utility detection.

300D	300 MHz antenna, “deep” viewing depth. Range 300 ns.
300S	300 MHz antenna, “shallow” viewing depth. Range 150 ns.
200D	200 MHz antenna, “deep” viewing depth. Range 300ns.
200S	200 MHz antenna, “shallow" viewing depth. Range 150 ns.
120D	120 MHz standard antenna, “deep” viewing depth. Range 400 ns.
120S	120 MHz standard antenna “shallow” viewing depth. Range 200 ns.
100D	100 MHz antenna normal transmitter power, “deep” viewing. Range 500 ns.
100S	100 MHz antenna normal transmitter power “shallow” viewing. Range 250 ns.
100HP	100 MHz antenna with high power transmitter. Range 500 ns.
100VHP	100 MHz antenna with very high power transmitter. Range 500 ns.
80MHz	80 MHz folded bow-tie antenna. Range 1000 ns.
LF120CM	Low Frequency antenna 1.2m length. Range 250 ns.
LF240CM	Low Frequency antenna length 2.4m. Range 500 ns.
LF360CM	Low Frequency antenna length 3.6m. Range 750 ns.
LF480CM	Low Frequency antenna set to a length of 4.8m. Range 1000 ns.
LF600CM	Low Frequency antenna set to a length of 6.0m. Range 1000 ns.
BH120	Borehole antenna frequency 120 MHz. Range 500 ns.
BH300	Borehole antenna frequency 300 MHz. Range 300 ns.

Common Setup Parameters Independent Of Antenna Used

The following parameters are common to all **pre-loaded setup** files.

Output Disk: *OFF*
Output Print: *OFF*
Output Display: *LINESCAN*
Display Color Table: *2*
Display Color Transform: *1*
Dielectric Constant: 0
Units: Meters
Screen: Full
2D Grid: OFF
Playback: Clear Processing

Setup Parameters Dependent On Antenna To Be Used

2500HS

This setup is for the 2500 MHz Horn antenna operated at high data acquisition speed. Maximum data acquisition speed 80kph (50mph) with a sample interval of 0.4m. Depth of viewing window is approximately 60cm (assuming a dielectric constant of 5).

Data Collection Mode: Survey Wheel
Range: 10ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 4
Vertical High Pass Filter: 300 MHz
Vertical Low Pass Filter: 5000 MHz
Scans per second: 64
Horizontal Smoothing: 0 scans
Survey Interval: 0.4m
Distance Mark: 50m
Transmit Rate: 64 KHz

2500HHR

This setup is for the 2500 MHz Horn antenna for high horizontal resolution road evaluation. Maximum data acquisition speed 11kph (7mph) with a horizontal sample interval of every 1 cm. Depth of viewing window is approximately 60cm (assuming a dielectric constant of 5).

Data Collection Mode: Survey Wheel
Range: 10ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 4
Vertical High Pass Filter: 300 MHz
Vertical Low Pass Filter: 5000 MHz
Scans per second: 64
Horizontal Smoothing: 0 scans
Survey Interval: 5cm
Distance Mark: 5m
Transmit Rate: 64 KHz

1500

Configures the 1500 MHz (5100) antenna for bridge and concrete surveys using automatic processing modules in RADAN NT (Bridge and Concrete Assessment).

Data Collection Mode: Survey Wheel
Range: 10 ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 1
Vertical High Pass Filter: 250 MHz
Vertical Low Pass Filter: 5000 MHz
Scans per second: 64
Horizontal Smoothing: 0 scans
Survey Interval: 0.0 m
Distance Mark: 50 m
Transmit Rate: 64 KHz

1500_2

A high gain setup for the 1500 MHz (5100) antenna for visual inspections.

Data Collection Mode: Survey Wheel
Range: 12 ns
Samples per Scan: 512
Resolution:16 bits
Number of gain points: 4
Vertical High Pass Filter: 1000 MHz
Vertical Low Pass Filter: 3000 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Survey Interval: 0.0 m
Distance Mark: 50m
Transmit Rate: 64 KHz

1000HS

This setup is for the 1000 MHz Horn antenna at high data acquisition speed. Maximum data acquisition speed 80kph (50mph). Depth of viewing window is approximately 1m (assuming a dielectric constant of 5).

Data Collection Mode: Survey Wheel
Range: 20ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 4
Vertical High Pass Filter: 200 MHz
Vertical Low Pass Filter: 2000 MHz
Scans per second: 64
Horizontal Smoothing: 0 scans
Survey Interval: 0.4m
Distance Mark: 50m
Transmit Rate: 64 KHz

1000 HHR

This setup configures the 1000 MHz Horn antenna for high horizontal resolution road evaluation. Horizontal sample interval every 1cm. Maximum data acquisition speed 11kph (7mph). Depth of viewing window is approximately 1m (assuming a dielectric constant of 5).

Data Collection Mode: Survey Wheel
Range: 20ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 4
Vertical High Pass Filter: 200 MHz
Vertical Low Pass Filter: 2000 MHz
Scans per second: 64
Horizontal Smoothing: 0 scans
Survey Interval: 5cm
Distance Mark: 5m
Transmit Rate: 64 KHz

1000TAD - Concrete And Roadway Evaluation

1000 MHz standard antenna. Depth of viewing window is approximately 1m assuming a dielectric constant of 5. With an antenna traverse speed of approximately 32cm per second, the horizontal sampling is 1 scan per cm.

Data Collection Mode: Continuous
Range: 15ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 4
Vertical High Pass Filter: 250 MHz
Vertical Low Pass Filter: 2000 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 64 KHz

1000TAS - Concrete and Roadway Evaluation

1000 MHz standard antenna. Depth of viewing window is approximately 50cm assuming a dielectric constant of 5. With an antenna traverse speed of approximately 32cm per second, the horizontal sampling is 1 scan per cm.

Data Collection Mode: Continuous
Range: 8ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 4
Vertical High Pass Filter: 250 MHz
Vertical Low Pass Filter: 2000 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 64 KHz

900TAVD - Shallow Archeological And Airport Runway Investigations

900 MHz antenna. Depth of viewing window is approximately 2m assuming a dielectric constant of 5. With an antenna traverse speed of approximately 50cm per second, the horizontal sample interval is approximately 2cm.

Data Collection Mode: Continuous
Range: 30ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 4
Vertical High Pass Filter: 100 MHz
Vertical Low Pass Filter: 1800 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 64 KHz

900TAD - Concrete, Roadway And Runway Evaluations

900 MHz antenna. Depth of viewing window is approximately 1m assuming a dielectric constant of 5. With an antenna traverse speed of approximately 32cm per second, the horizontal sampling is 1 scan per cm.

Data Collection Mode: Continuous
Range: 15ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 4
Vertical High Pass Filter: 100 MHz
Vertical Low Pass Filter: 1800 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 64 KHz

900TAS

900 MHz antenna. Depth of viewing window is approximately 50cm assuming a dielectric constant of 5. With an antenna traverse speed of approximately 32cm per second, the horizontal sampling is 1 scan per cm.

Data Collection Mode: Continuous
Range: 8ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 4
Vertical High Pass Filter: 100 MHz
Vertical Low Pass Filter: 1800 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 64 KHz

500D

500 MHz antenna. Depth of viewing window is approximately 5m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 100ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 1000 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 64 KHz

500S

500 MHz antenna. Depth of viewing window is approximately 3m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 60ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 1000 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 64 KHz

500DPH

500 MHz dual-power antenna on high transmit power setting. Depth of viewing window is approximately 5m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 100ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 1000 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 32 KHz

500DPL

500 MHz dual power antenna on low transmit power setting. Depth of viewing window is approximately 5m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 100ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 1000 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 32 KHz

400D

400 MHz antenna. Depth of viewing window is approximately 5m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 100ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 800MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 64 KHz

400S

400 MHz antenna. Depth of viewing window is approximately 3m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 60ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 800 MHz
Scans per second: 32
Horizontal Smoothing: 4 scans
Transmit Rate: 64 KHz

300D

300 MHz antenna. Depth of viewing window is approximately 15m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 300ns
Samples per Scan: 1024
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 1000 MHz
Scans per second: 32
Horizontal Smoothing: 5 scans
Transmit Rate: 64 KHz

300S

300 MHz antenna. Depth of viewing window is approximately 7m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 150ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 1000 MHz
Scans per second: 32
Horizontal Smoothing: 5 scans
Transmit Rate: 64 KHz

200D

200 MHz antenna. Depth of viewing window is approximately 15m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 300ns
Samples per Scan: 1024
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 400 MHz
Scans per second: 32
Horizontal Smoothing: 5 scans
Transmit Rate: 64 KHz

200S

200 MHz antenna. Depth of viewing window is approximately 7m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 150ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 400 MHz
Scans per second: 32
Horizontal Smoothing: 5 scans
Transmit Rate: 64 KHz

120D

120 MHz standard antenna. Depth of viewing window is approximately 20m assuming a dielectric constant of 9. Note: The 120 MHz antenna is unshielded.

Data Collection Mode: Continuous
Range: 400ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 240 MHz
Scans per second: 32
Horizontal Smoothing: 5 scans
Transmit Rate: 64 KHz

120S

120 MHz standard antenna. Depth of viewing window is approximately 10m assuming a dielectric constant of 9. Note: The 120 MHz antenna is unshielded.

Data Collection Mode: Continuous
Range: 200ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 240 MHz
Scans per second: 32
Horizontal Smoothing: 5 scans
Transmit Rate: 64 KHz

100D

100 MHz antenna normal transmitter power. Depth of viewing window is approximately 25m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 500ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 25 MHz
Vertical Low Pass Filter: 200 MHz
Scans per second: 16
Horizontal Smoothing: 5 scans
Transmit Rate: 64 KHz

100S

100 MHz antenna normal transmitter power. Depth of viewing window is approximately 12m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 250ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 25 MHz
Vertical Low Pass Filter: 200 MHz
Scans per second: 16
Horizontal Smoothing: 5 scans
Transmit Rate: 64 KHz

100HP

100 MHz antenna with high power transmitter. Depth of viewing window is approximately 25m assuming a dielectric constant of 9.

Data Collection Mode: Continuous
Range: 500ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 25 MHz
Vertical Low Pass Filter: 200 MHz
Scans per second: 16
Horizontal Smoothing: 5 scans
Transmit Rate: 32 KHz

100VHP

100 MHz antenna with very high power transmitter. Depth of viewing window is approximately 25m assuming a dielectric constant of 9.

Data Collection Mode: *Continuous*
Range: 500ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 25 MHz
Vertical Low Pass Filter: 200 MHz
Scans per second: 16
Horizontal Smoothing: 5 scans
Transmit Rate: 16 KHz

80MHz

80 MHz folded bow-tie antenna. Note: The 80 MHz antenna is unshielded.

Data Collection Mode: Continuous
Range: 500ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 25 MHz
Vertical Low Pass Filter: 200 MHz
Scans per second: 32
Stacking: 32 scans
Transmit Rate: 32 KHz

LF120CM

Low Frequency antenna 1.2m length. Note: The MLF antennas are unshielded.

Data Collection Mode: Point
Range: 250ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 160 MHz
Scans per second: 32
Stacking: 32 scans
Transmit Rate: 32 KHz

LF240CM

Low Frequency antenna length 2.4m

Data Collection Mode: Point
Range: 500ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 15 MHz
Vertical Low Pass Filter: 90 MHz
Scans per second: 32
Stacking: 32 scans
Transmit Rate: 32 KHz

LF360CM

Low Frequency antenna length 3.6m

Data Collection Mode: Point
Range: 750ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 10
Vertical Low Pass Filter: 60
Scans per second: 32
Stacking: 32 scans
Transmit Rate: 32 KHz

LF480CM

Low Frequency antenna set to a length of 4.8m

Data Collection Mode: Point
Range: 1000ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 5
Vertical High Pass Filter: 6
Vertical Low Pass Filter: 40
Scans per second: 32
Stacking: 32 scans
Transmit Rate: 32KHz

LF600CM

Low Frequency antenna set to a length of 6.0m

Data Collection Mode: Point
Range: 1000ns
Samples per Scan: 512
Resolution: 8 bits
Number of gain points: 5
Vertical High Pass Filter: 1
Vertical Low Pass Filter: 50
Scans per second: 32
Stacking: 32 scans
Transmit Rate: 32 KHz

BH120

Borehole antenna frequency 120 MHz. Note: The borehole antennas are unshielded.

Data Collection Mode: Point
Range: 500ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 30 MHz
Vertical Low Pass Filter: 240 MHz
Scans per second: 32
Stacking: 32 scans

BH300

Borehole antenna frequency 300 MHz.

Data Collection Mode: Point
Range: 300ns
Samples per Scan: 512
Resolution: 16 bits
Number of gain points: 5
Vertical High Pass Filter: 38 MHz
Vertical Low Pass Filter: 600 MHz
Scans per second: 32
Stacking: 32 scans

Appendix B: Selecting The Proper Antenna

GSSI offers many antennas of different frequencies and functions that can be operated with the SIR-2000. There will one or two GSSI antennas best suited for your application. It is important that you select the correct antenna for your application in order to obtain the best possible results.

Your depth of interest for a particular application will determine the correct antenna to use. The deeper the depth of interest, the lower the frequency of antenna you should use. The higher the antenna frequency, the greater the resolution or ability to see smaller targets.

For best results, you should select the highest frequency antenna that will cover your depth of interest (Table B1). For example, if you were looking for pipes down to 2.5 meters depth, both the 200MHz and 400MHz antennas are capable of penetrating to that depth. In most cases, you should select the 400MHz antenna because it provides better resolution. If you do not have that frequency antenna available, you can try the next lower frequency antenna (in this example the 200MHz), but you should realize that it will have decreased ability to see small targets.

Table B1

Best GSSI antennas to use for a given depth range of investigation

Depth Range of Interest	Best antenna to use	Second Choice
0-0.5m(0-1.5ft)	1500MHz	900MHz
0-1m (0-3ft)	900MHz	400MHz
0-2.5m (0-8ft)	400MHz	200MHz
0-9m (0-30ft)	200MHz	100MHz
0-20m (0-60ft)	Subecho-70	100MHz
0- >20m (0- >60ft)	Subecho-40	100MHz

Note: GSSI is constantly developing new antennas that may not be listed above. Please contact us to obtain most recent information on available antennas.

Appendix C: SIR System-2000 Specifications

Hardware

IDE Internal Hard Drive:	minimal capacity 1.4 GB.
Display:	21cm color active matrix LCD VGA for real-time display, 640 x 480 pixels.
Inputs/Outputs:	1 Antenna Input (including survey wheel) 1 12VDC Power Input 1 Keyboard (PC/AT-compatible) connector 1 Parallel Connector 1 Serial Connector 1 Audible Warning Beeper (speaker) 3 LED Indicators, 2 Power, 1 hard drive
Printer:	Optional thermal plotter for real-time hard copy of wiggle-trace or grayscale linescan data.

Software

Data Collection:	Continuous profile, survey wheel-controlled or stacking (point collection) modes. DISPLAY MODE: User-selected; color/grayscale linescan, wiggle trace or oscilloscope data formats. Menus and system parameters.
Range Gain:	Automatic or user-selected; range gain function **prior** to digitization for maximum system dynamic range.
Data Transfer:	Bi-directional parallel port. Optional serial transfer.

Electrical

Transducer:	Operates with any GSSI model transducer.
Range:	6-3000 nanoseconds full scale, user selectable, fixed ranges of 8,15, 25, 35, 50, 70, 100, 150, 200, 250, 300, 400, 500, 750, 1000.
Pulse repetition rate:	Automatically selected, 8 to 64 KHz.
Sampling:	Automatically or manually selected, 128, 256, 512, 1024, or 2048 samples/scan.
Quantization:	8 or 16-bit
Input Power:	12VDC from vehicle or belt mounted, rechargeable battery with operating range of 10-12.5 volts, 100 watts.

Environmental

Operating Temperature:	0^{o} C to 40^{o} C (32 F to 104 F) external.
Relative Humidity:	0-100%
Storage Temperature:	-25^{o} C to 50^{o} C (-20^{o} F to 122^{o} F)
Water:	Splash-proof - not intended to be immersed
Dust:	All sensitive components are housed in dust-resistant enclosures.

Mechanical

Dimensions:	13.5” x 11.5” x 6”
Weight:	15 lbs

Appendix D: Data Transfer Utility For Windows 95 and Windows NT

Disclaimer

This software is provided as a courtesy to our customers, and therefore is distributed on an "as-is" basis, with no warranties, implied or otherwise. There is no support provided by GSSI for this product, and it is the responsibility of the customer to determine the suitability of this application for their intended purpose. In using this software, the customer acknowledges and accepts the terms of disclaimer.

Introduction

Overview:

The Data Transfer Utility allows the user to transfer data from a SIR System-2000, SIR System-2, SIR System-2P, SIR System-10A+, SIR System-10B, or SIR System-10H to a personal computer. Transfers from all other systems are not supported.

Compatibility:

This software requires that the user be running either Windows 95 or higher or Windows NT version 4.0 or higher. This software is not compatible with Windows 3.1 or Windows for Workgroups. The system receiving the data must also contain an EPP, Bi-directional, or PS/2 parallel port. Ports configured for Output Only, or ECP will not work.

Warning: Do not attempt to transfer data through your Radan or Radprint security key. Doing so will damage the key, rendering it unable to function properly.

Using the Data Transfer Utility

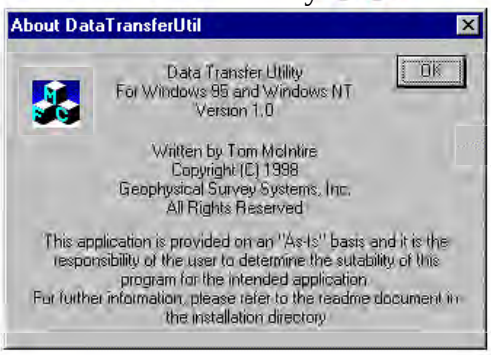
Setup:

To install the Data Transfer Utility, run the SETUP.EXE program in the directory containing the software. This setup program will guide the user through the installation process. Upon completion of the setup program, the user will be required to reboot the computer in order for changes to take effect. If installing the software in Windows NT, the account being used must have full administrative privileges. If the account used does not have full privileges, the software will not function, and will need to be reinstalled.

Running the Software:

***Note*:** It is recommended to deactivate the screen savers on the computer as they may interrupt data transfer (Right-click on the desktop, select Properties in the pop-up menu that appears, then the Screen Saver tab. Choose NONE and click OK).

To run the software, choose Data Transfer Utility  from the GSSI Group in the Programs



menu. Upon selecting this, a dialog box will appear, as shown below in Figure 3.

Figure 3: The About Data Transfer Utility Dialog Box.

After acknowledging the dialog, the user will be presented with the main program dialog. This will look similar to the one shown below in Figure 4.

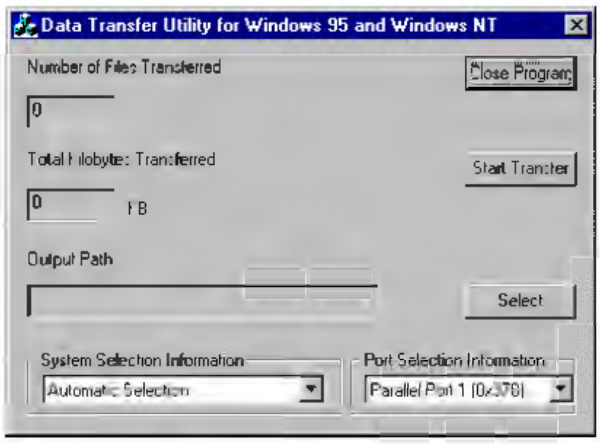


Figure 4: Main program dialog box.

To transfer data, do the following:

1. Choose the directory to transfer data to by pressing the *Select* button to the right of the Output Path field. This will run a directory picker, which will allow the user to select a directory.
2. Next select the files on the SIR System to be transferred and start transfer on the SIR System.
3. Press *Start Transfer* in the dialog. This will create a temporary directory in the directory selected for data transfer. The files will be transferred to this temporary directory, and then moved to the directory selected for data transfer.
4. If files already exist in the destination directory which have the same name as the files just transferred, the user will be given the opportunity to do one of the following:

- Delete the original (old) file on the computer and replace it with the file just transferred.
- Specify a new name for the file just transferred to the computer.
- Delete the file just transferred to the system, leaving the old file intact.

If all the above are rejected, both files are left intact, and the process starts over. As a result, the user is forced to choose one of the above options.

At this point, all the data is in the specified destination directory and the temporary directory is removed automatically.

Sources of Error within Windows NT:

If the giveio.sys device driver is not installed on the system correctly and started, the system will give an error, similar to the one shown in Figure 3, immediately after the About dialog box is dismissed.

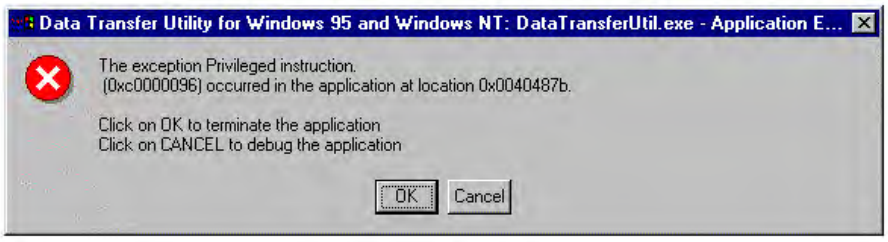


Figure 5: Error when giveio.sys is not loaded and running.

If this occurs, the application needs to be reinstalled, being sure that the user account being used has full administrative privileges. (Please note: the numbers displayed in the error message will vary).

This will also happen if *giveio.sys* is not placed in the appropriate folder. Make sure a copy of *giveio.sys* is present in C:\WINNT\System32\Drivers and restart the computer.

Sources of Error within Windows NT and Windows 95:

If the user attempts to transfer data to a directory which they do not have permission to write data to, ie: a network read-only share, or a protected directory within Windows NT, the following error will occur (as shown in Figure):

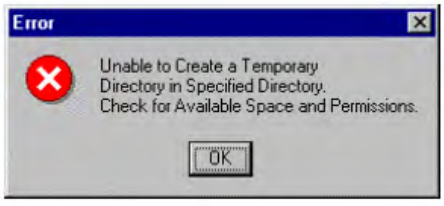


Figure 6: Error message is the disk cannot be written to.

Appendix H

UXO Standard Operating Procedures

Explosives Management Plan

This section outlines the explosives management procedures Parsons and all subcontractors will use to perform the Removal Action at the Seneca Army Depot.

Acquisition

Parsons holds a BATF permits to purchase and use explosives (see Figures 3.1 and 3.2). This permit will be posted on site and will be available for local, state, or federal inspection. Parsons will store the demolition material on site in an existing DDESB-approved explosive storage magazine existing onsite at Seneca Army Depot. Primary responsibility, accountability, and use of the explosives will remain with Parsons unless custody is transferred to the Government or another contractor with a current BATF explosive license.

Description and Estimated Quantities

When required, Parsons will order and stock an initial quantity of not more than 50 pounds net explosive weight (NEW) of commercial counter charges, initiating explosives, and venting charges for disposal and demilitarization operations. Based on usage and demand, the quantity in stock may increase, but at no time will storage quantities exceed 100 pounds Net Explosives Weight. Parsons will purchase explosives from a local licensed explosives distributor, who will deliver the demolition material to the site. The SUXOS will be authorized to request and receive explosives from the explosives distributors.

Listing of Proposed Explosives

The types of explosives that may be used are:

- Cast booster (1/2 – 1 pound);
- Perforator charge (32 gram shape charge);
- Detonating cord (50 & 80 grain);
- Blasting caps (non-electric);
- Safety fuze and fuze igniters;
- Binary explosives; and
- Nonel® Shock Tube.

Receipt Procedures

Parsons SUXOS will strictly control access to all explosives. All receipts, issues, turn-ins, and inventories of explosives will be properly documented and verified, through physical count, by the SUXOS and UXOQCS.

Records Management and Accountability

All original explosive records will be forwarded to Parsons Boston for archive in accordance with BATF regulations and requirements. Copies of all records will be maintained on site by the site supervisor and will be available for inspection by authorized agencies. Explosive items will be tracked by their respective lot number until the items are expended or transferred to government control and accountability or are returned to the distributor.

Authorized Individuals

Parsons is required to provide explosives distributors with documentation of individuals authorized to request and receive explosives. The individuals authorized to receive and issue explosives are the Parsons SUXOS and, in some cases when the SUXOS is not available, either the Tech III demolition supervisor or the Parsons UXOQCS. The SUXOS will designate in writing the individual(s) authorized to transport and use explosives.

Certification

The SUXOS and UXO Technician III team leader performing demolition will sign and date the Explosives Usage Form (see **Appendix C, Page C-40**) certifying that the explosives were used for their intended purpose.

Procedures for Receipt of Explosives

On receipt, the type, quantity, and lot number of each explosive item will be checked against the manifest and recorded on the Magazine Data Card (see **Appendix C, Page C-41**). The original receipt documents and an inventory will be maintained on file by the site supervisor. The Magazine Data Card will remain in the magazine with the explosive items and be annotated and updated upon each issue, receipt, and inventory.

Procedures for Reconciling Receipt Documents

The SUXOS will reconcile the delivery shipping documentation with the requested amounts ordered and received. Any shortages or overages will be reported to the USA Environmental PM, who will contact the explosives distributor and reconcile any differences. In addition he will notify the Parsons site and project managers.

Inventory Procedures

Explosives will be inventoried at least weekly by the UXOQCS and the SUXOS. Complete inventories will also be conducted after any issues/turn-ins of demolition material.

Storage Facility Physical Inventory Procedures

The SUXOS will strictly control access to all explosives. All issues and turn-ins of explosives will be properly documented and verified, through physical count, by the SUXOS and UXOQCS. On receipt, the type, quantity, and lot number of each explosive item is recorded on the Magazine Data Card (see **Appendix C, Page C-41**).

The SUXOS will review all requests for explosives from the individual operating sites and only sufficient explosives for the day's operations will be issued. Issues of explosives are recorded on Explosives Usage Records entries (see **Appendix C, Page C-40**) and deducted from the Magazine Data Card(s) and annotated in the daily journal. This procedure will ensure that the issued explosives are accounted for while they are in the possession of individual users. The end user of explosives shall certify on the Explosives Usage Record that the explosives were used for their intended purpose. Entries made on the Explosives Usage Records and Magazine Data Cards will be verified through physical count by the demolition team UXO Technician III when drawing or turning in the explosives and verified by the UXOQCS.

At the end of each disposal operation, the UXOQCS and the demolition team UXO Technician III will reconcile the entries on each Explosives Usage Record and will turn these records over to the SUXOS. The record of ordnance items destroyed with the explosives consumed will be kept in the SUXOS daily log.

Entries made on the Explosives Usage Records and Magazine Data Cards will be verified through physical count of the amount being drawn by the demolition team UXO Technician III when drawing or turning in the explosives, and the UXOQCS will verify the record.

Procedures for Reconciling Inventory Discrepancies

The SUXOS and UXOQCS will be responsible for performing a weekly inventory of the explosives within the magazine. If there is a discrepancy between the inventory and the volume of explosives within the magazine, then they will review the magazine Data Card and Explosives Usage Record to see if the inventory records are current. If the records review does not reconcile the discrepancy, it will be reported to the USACE safety specialist, contracting officer (CO), and USA Environmental PM for investigation. In addition, the Parsons site and project managers will be notified.

Reporting Loss or Theft of Explosive Materials

If it is confirmed that ordnance or explosives are missing, then the SUXOS will contact the CO immediately by telephone and in writing within 24 hours. The USACE site safety specialist Parsons site and project managers will be notified following the notification of the CO. Parsons will notify BATF and immediately begin an investigation. Local authorities will be notified, and a written report will be issued within 24 hours.

Procedures for Return to Storage of Explosives Not Expended

Explosives that were issued for use but were not expended will be returned daily to the magazines at the completion of disposal operations. The demolition team UXO Technician III will return

the unused explosives to the storage magazine and record the items on the Magazine Data Card and Explosives Use Record.

Physical Security of Storage Facilities

In accordance with DID 6055-9 STD and EM 1110-1-4009. The magazine storage area (MSA) will be inspected each workday by the SUXOS and UXOSO or UXOQCS to ensure the integrity of the enclosure.

Transportation of Explosives

Transportation of demolition material (explosives) will comply with all federal, state, and local regulations. Placards will be used on all vehicles transporting explosives and a 25mph speed limit will be observed for any vehicle transporting demolition materials. Parsons will use the most expeditious route when transporting demolition material.

Procedures for Transportation from Storage to Disposal Location

Transportation of explosives on the former Seneca Army Depot will not require travel on public highways. However, placarding and inspections will be conducted in accordance with the Parsons Explosives Storage and Transportation SOP. No public roads will be traveled with explosives during the removal Action at Seneca Army Depot. The Explosive Vehicle Inspection form (see **Appendix C, Page C-42**) will be used for the transporting vehicle every time explosives are transported within the limits of Seneca Army Depot.

Explosive Transportation Vehicle Requirements

Explosives will be transported in closed vehicles whenever possible. The load shall be braced and, except when in closed vehicles, covered with a fire-resistant tarpaulin or in an appropriate shipping container. Minimum vehicle requirements include:

- Vehicles transporting explosives or UXO/MPPEH will be inspected daily using the Explosive Vehicle Inspection Form (see **Appendix C, Page C-42**), as applicable, and will be properly placarded;
- Vehicle engine will not be running when loading/unloading explosives;
- Vehicle will be chocked to prevent movement while loading;
- Beds of vehicles will have either a wooden bed liner, dunnage, or sand bags to protect the explosives from contact with the metal bed and fittings; and
- Vehicles transporting explosives will have a first aid kit, two 10 BC fire extinguishers, and a means of communication with the UXOSO.

Disposal of Remaining Explosives

BATF requires an accounting of all explosives purchased and used; therefore, at project completion, all unused explosives will either be disposed of by detonation or custody, and accountability will be transferred to an incoming contractor, a government agency, or returned to the distributor.

STANDARD OPERATING PROCEDURE

FOR

FOR BACKHOE OPERATIONS

1.0 BACKGROUND

Backhoes are used at Fort Ord Site to excavate during investigation of subsurface magnetic anomalies, during clearing of rodent nests and for minor road repair to facilitate site access and egress.

2.0 SCOPE

This Standard Operating Procedure (SOP) contains information specific to the former Fort Ord site. It includes copies of the Operators Manual and the Lubrication and Maintenance Guide for the Ford 575D backhoe. It may also include manuals and publications relevant to other backhoes that may be leased, purchased or otherwise employed on the site. It is incumbent upon all designated operators to familiarize themselves with this SOP and to periodically review it an effort to remain current with safe, productive backhoe procedures.

3.0 OPERATIONS

USA Environmental employees who operate backhoes on the former Fort Ord Site will be qualified through on-the-job training (OJT); equivalent OJT documented through previous employment or experience or through documented formal training. When engaged in backhoe operations the operator will perform daily inspection and maintenance functions and operate the backhoe as directed. S/He will also conduct OJT of other operators at the team leader's discretion.

3.1 Personnel Protective Equipment (PPE)

Modified Level D PPE will be required for personnel engaged in backhoe operations. Clothing items will be:

- Coveralls or work clothing as prescribed;
- Work gloves, leather or canvas, as appropriate
- Safety glasses - as wind conditions and airborne particulate matter dictates;
- Hard hats;
- Work Boots (Sturdy and of sufficient height to aid in ankle support);
- Hearing Protection: Noise Attenuating Helmet or earplugs will be worn by anyone within 25 feet of the Ford 575 D backhoe while it is operating. Hearing protection for any other backhoe brought on site will be determined through a Noise Survey (sound level meter survey); and

- Dust Masks - as wind conditions and airborne particulate matter dictates.

NOTE: *If the backhoe is being used for the clearance of rat nests to facilitate a magnetometer sweep PPE will be IAW the USA Hantavirus SOP.*

3.2 General Safety Precautions

The following lateral distances will be maintained when operating a backhoe on a MRS site:

- 200 feet from non-UXO trained personnel;
- 200 feet from another backhoe; and
- 200 feet from other UXO personnel conducting manual, intrusive operations.

These distances may be reduced or extended by the CESPK Safety Specialist based on an assessment of site history, expected MEC, terrain features or other such factors that may apply. The backhoe will not be operated without a spotter. This includes using the front and rear attachments and backing the tractor. Prior to starting an excavation, a safety arc will be etched in the ground with the rear boom, fully extended. If operating on a hard surface, the safety arc will be marked with bright spray paint. Prior to anyone entering the safety arc, the operators will:

- Swing the boom arm fully to one side;
- Lower the bucket to the ground;
- Return the engine to idle speed; and
- Hold her/his hands clear of the controls or in the "Hands Up" position.

3.2.1 Equipment Safety Precautions

See the Ford Operators Manual, issue 3/94, pages ii through v.

3.3 Team Composition

The UXO Supervisor will serve as a safety observer and director for other team personnel and all members of the backhoe team will be UXO qualified. The minimum team make-up will be:

- One operator;
- One ground person; and
- One UXO Supervisor/Team Leader.

3.3.1 Ground Personnel

Team members working on a backhoe team will be qualified through OJT and will perform such tasks as magnetometer checks, manual excavation and checks of the hole.

3.4 Training

Training will be documented in UXO Supervisors field notebooks and on USA Environmental on-site records.

3.5 General Operational Procedures

The operator will have a radio in place so s/he can monitor radio transmissions while driving the backhoe to and from excavation sites. Prior to shutting off the tractor engine the operator should let the engine run at idle speed for a few minutes to allow the turbo charger to cool. Prior to excavation operations the UXO Supervisor shall establish/review hand signals with all members to the team. The backhoe will not be used to excavate closer than 12 inches from MEC. Removed dirt will be placed at least 2 feet from the expected edge of the excavation, and on the uphill side when working on a slope. Excavations will not be deeper than 4 feet without authorization from the CESPK Safety Specialist. Such excavations require the Site Safety Officer to determine step/slope requirements.

OE SECTOR
Standing Operating Procedure (SOP)

Barricade Operations

PARSONS
5390 Triangle Parkway, Suite 100
Norcross, Georgia 30092

Revision No. 1
February 2005

1.0 PURPOSE

The use of the Barricade System (BS), consisting of the Open Front Barricade (OFB), Enclosed and Miniature Open Front Barricade (MOFB), will be selected based on its mitigation capabilities and applicability to the specific munitions response (MR) site. The applicable BS is to be used when non-essential personnel and/or structures are within the established exclusion zone, based on the sites most probable munitions (MPM).

2.0 SCOPE

All personnel performing operations utilizing the BS shall comply with this SOP, which is not a stand-alone document, and shall become familiar with associated documents and/or manuals related to its use.

3.0 REGULATORY REFERENCES

- CEHNC EP 385-1-95a, Basic Concepts and Considerations for Ordnance and Explosive Operations
- HNC-ED-CS-S-99-1, Open Front and Enclosed Barricades
- HNC-ED-CS-S-98-8, Miniature Open front Barricade

4.0 RESPONSIBILITIES

4.1 UXO Safety Officer

The UXOSO ensures that all operations involving the BS are being conducted in accordance with the Site Specific Work Plan, and this SOP. The UXOSO will ensure that all personnel using the BS are appropriately trained on the hazards associated with its use and to document the training.

4.2 UXO Tech III (UXO Team Leader)

The UXO Tech III is responsible for the maintenance, proper use and inspection of the BS and will ensure that all team members receive a safety briefing prior to employing the selected BS. He will also ensure that all team members are familiar with this SOP and its requirements when employing the BS.

5.0 OPERATIONS

The BS will be used in the following manner:

- The BS will be used to investigate suspect ordnance items in areas where establishment of the minimum safe distance (MSD) is not possible, i.e., near the installation boundary or areas in close proximity to occupied structures, roadways or rail lines.

- The BS will be erected with the suspect UXO a minimum of six inches inside of the open front. The enclosed end of either the MOFB or the OFB will face the area to be protected.

- The plates will be installed one at a time, and slowly lowered into the BS, not dropped, being cautious not to pinch fingers while installing the plates.

- The BS will be completely erected prior to any investigation or excavation of the suspect item. The BS will be transported to and from the site on a trailer or in a pickup truck and moved between excavation sites by Bob-Cat or backhoe when terrain and vegetation permit.

- When transporting the BS by hand, a minimum of four (4) individuals will be used and to minimize weight, the aluminum plates will be removed.

- The mainframe and plates will be inspected prior to each use for damage, cracks, dents, bends, etc.

- The BS will not be used within 200 feet of non-essential personnel or occupied structures.

- Only one person will occupy the BS during excavations and investigations.

WARNINGS:

- The largest munition that the MOFB is designed for is the M-374, 81mm mortar, HE.
- The largest munition that both the OFB and Enclosed Barricades are designed for is the M-107, 155mm projectile, HE.
- Care should be used when installing and removing plates, severe injury to fingers can occur if care and proper clearance is not maintained. An overhead hazard may exist when entering and exiting the BS due to head clearance.

6.0 PERSONNEL PROTECTIVE EQUIPMENT

Personnel Protective Equipment (PPE), those handling the BS will consist of leatherwork gloves, steel toed boots and if the plates are being lifted any higher than shoulder height hard hats will be worn. Additional PPE requirements will be in accordance with the Site Specific Work Plan.

STANDARD OPERATING PROCEDURE
FOR
CHIPPING OPERATIONS

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide the minimum procedures and safety and health requirements applicable to the conduct of chipping operations in areas that are considered environmentally sensitive.

2.0 SCOPE

This SOP applies to all personnel involved in the conduct of chipping operations either using a disk-type or rotary drum type.

3.0 REGULATORY REFERENCES

- Parsons Corporate Safety and Health Program;
- OSHA General Industry Standards, 29 CFR 1910;
- OSHA Construction Standards, 29 CFR 1926;
- USACE EM 385-1-1, Safety and Health Requirements Manual;
- AR 385-10, Army Safety Program; and
- Operators Manual and Manufacturers Recommendations.

4.0 RESPONSIBILITIES

4.1 Program Manager (PM)

The PM is responsible for ensuring availability of resources required to safely implement this SOP.

4.2 Field Operations Manager (FOM)

The FOM is responsible for incorporating this SOP in plans, procedures, and training.

4.3 UXO Safety Officer (UXOSO)

The UXOSO ensures that all chipping operations are being conducted in a safe manner, in accordance with the Programmatic Work Plan, Site Specific Work Plan, and this SOP.

4.4 Chipper Team Leader

The chipper team leader is responsible for the daily maintenance, upkeep, and repair of the machine, and certification of operator personnel.

5.0 CHIPPING OPERATIONS

5.1 General

Chipping is required whenever vegetation removal is being conducted in the Habitat Management Area (HMA). In addition, it may be necessary to conduct chipping to improve ground visibility and safety.

5.2 Chipper Operation

The chipper will be manned by two brush feeders (laborers), one on each side of the chipper. When feeding material into the chipper, feeders must exercise care not to place hands, or any other parts of the body, or loose clothing on the feed table when the chipper is in operation. Care is taken not to reach past the "SAFE" point established on the feed table/chute. This point varies between chipping machines and will be identified to all personnel.

- A push stick of material consumable by the chipper will be available, one on either side of the chipper, for pushing material into the chipper when necessary to probe beyond the safe point.

- Two or more brush draggers will be employed to drag brush to the feeders. The draggers will trim the brush as necessary to fit into the chipper, and pass it to the feeders.

- Limbs and woodstock 3" or greater in diameter need not be chipped. These items can be left in the field as a source of habitat for bugs, salamanders, and other creatures.

- The chipper Team Leader must not involve himself in the chipping operation. He must oversee the operation with regard to safety, work progress, weather/wind conditions, materials being chipped, and other factors that impact on the operation.

- Poison Oak will not be chipped by itself. If it is entangled within brush, it will be chipped based on the Team leaders' discretion.

- Any time the chipper is operated while disconnected from the team vehicle, the chipper's wheels will be blocked or chocked to prevent it from rolling.

- Check fluid levels and gauges periodically and at every break.

5.3 Chipped Mulch

Mulch will, as much as possible, be spread over the area from which the original brush material was cut, and be limited to 3" in depth. Mulch will not be spread any closer than 5 feet from the roadsides whenever possible.

5.4 Field Sanitation

The team decontamination station will be located at least 50 feet upwind of the chipping operation. If the team vehicle is attached to the chipper, the team equipment in the pickup bed will be covered with a tarp or plastic sheet material.

5.5 Hearing Conservation

The first day, the noise level will be measured using an appropriate measuring device(s). Readings will be taken at the machine, as well as in the vicinity of the machine, and noise attenuation devices selected and issued.

6.0 PERSONAL PROTECTIVE EQUIPMENT (PPE)

Modified Level D PPE will be required for personnel engaged in chipping operations to include:

- Coveralls – appropriately taped at ankles and openings;
- Surgical/Inner gloves;
- Leather or Canvas work/outer gloves;
- Leather Gauntlets;
- Work Boots – Leather or suitable material;
- Tyvek Hood when in poison oak;
- Hard Hats;
- Hearing Protection:
  - Brush Feeders will wear Noise Attenuating Helmets or Ear Plugs. Both will be worn in uninterrupted work period extends beyond 45 minutes.
  - Brush Draggers will wear Noise Attenuating Helmets or Ear Plugs.
- Eye Protection:
  - All personnel will wear safety glasses. Brush feeders will also wear face shields/screens.
  - At any time that dust is being generated, disposable dust masks will be worn.
- No one will approach within 35 feet of an operating chipper without the appropriate PPE and hearing protection.

7.0 TRAINING

All personnel who work on a chipping crew will be qualified and certified through machine specific, site specific and on-the-job training. This training will consist of:

- Mechanical operations and maintenance of the chipper;
- Features of the chipper and its operational limits and characteristics; and
- Safety parameters relevant to chipping operations.

OE SECTOR
Standing Operating Procedure (SOP)

Demolition Operations

PARSONS
5390 Triangle Parkway, Suite 100
Norcross, Georgia 30092

Revision No. 1
February 2005

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide the minimum procedures and safety and health requirements applicable to the conduct of demolition/disposal operations on sites contaminated with Munitions and Explosives of Concern (MEC).

2.0 SCOPE

This SOP applies to all site personnel, including contractor and subcontractor personnel, involved in the conduct of demolition/disposal operations on an MEC contaminated site. This SOP is not intended to contain all of the requirements needed to ensure complete compliance, and should be used in conjunction with project plans and applicable Federal, state and local regulations. Consult the documents listed in section 3.0 of this SOP for additional compliance issues.

3.0 REGULATORY REFERENCES

Applicable sections and paragraphs in the documents listed below will be used as references for the conduct of demolition/disposal operations:

- Parsons Corporate Safety and Health Program;
- EP 385-1-95a, Basic Safety Concepts and Considerations for OE Operations;
- EP 1110-1-17, Establishing a Temporary OB/OD Site for Conventional Ordnance and Explosives Projects;
- EP 1110-1-18, Ordnance and Explosives Response;
- EM 1110-1-4009, Ordnance and Explosives Response;
- USACE EM 385-1-1, Safety and Health Requirements Manual;
- DoD 4145.26-M, Contractor's Safety Manual for Ammunition and Explosives;
- DoD 6055.9-STD, DoD Ammunition and Explosives Safety Standards;
- AR 385-64, Ammunition and Explosive Safety;
- DA PAM 385-64, Ammunition and Explosives Safety Standards;
- TM 60A-1-1-31, EOD Disposal Procedures;
- AR 190-11, Physical Security of Arms, Ammunition and Explosives;
- ATF 5400.7, Alcohol Tobacco and Firearms Explosives Laws and Regulations; and
- Applicable sections of DOT, 49 CFR Parts 100 to 199.

4.0 Responsibilities

4.1 Project Manager

The Project Manager (PM) shall be responsible for ensuring the availability of the resources needed to implement this SOP, and shall also ensure that this SOP is incorporated in plans, procedures and training for sites where this SOP is to be implemented.

4.2 Senior UXO Supervisor

The Senior UXO Supervisor (SUXOS) will be responsible for assuring that adequate safety measures and housekeeping are taken during demolition activities, and shall visit

demolition locations to ensure that demolition operations are carried out in a safe, clean, efficient and economical manner**.**

4.3 UXO Technician III (Demolition Supervisor)

A designated UXO Tech III shall act as the Demolition Supervisor (DS). There may be more than one DS assigned to a project site due to conducting simultaneous operations and divergent sites. The demolition activities shall be conducted under the direct control of the DS, who will have the responsibility of supervising all demolition operations assigned to him. The DS shall be responsible for training all on-site UXO demolition personnel on his team regarding the nature of the materials handled, the hazards involved and the precautions necessary to conduct a safe demolition operation. The DS will also ensure that the Daily Operational Log, Demolition Shot Records and inventory records are properly filled and accurately depict the demolition events and demolition material consumption for each day's operations. The DS shall be present during all demolition operations.

4.4 UXO Safety Officer

The UXO Safety Officer (UXOSO) for the site is responsible for ensuring that all demolition operations are being conducted in a safe and compliant manner, and is required to be present during all demolition operations. The only exception to this rule is when the project site has multiple sites conducting concurrent munitions response (MR) operations, and it is impossible for the UXOSO to be present at each shot. In that event a demolition team safety officer will be designated. This individual will report to the UXOSO and assume the UXOSO's responsibilities at the designated demolition operation. In this situation, the UXOSO will conduct periodic safety audits of the demolition teams and assist the demolition team's safety officers in the performance of their duties. The UXOSO or demolition team safety officer will inspect the demolition shot(s) for hazards and then assisted by the DS and UXO Tech IIs, will inspect each demolition pit and an area of up to 250 feet in radius after each demolition shot to ensure that no kick-outs of hazardous MEC components or other hazardous items has occurred.

4.5 UXO Quality Control Specialist

The UXO Quality Control Specialist (UXOQCS) is responsible for inspecting, the Daily Operational Log, the Demolition Shot Record and the inventory of MEC and demolition material. The UXOQCS will check the pit/demolition site with a magnetometer and large metal fragments exceeding the pass/fail requirements of the SOW will be removed.

5.0 GENERAL OPERATIONAL AND SAFETY PROCEDURE

All personnel, including contractor and subcontractor personnel, involved in operations on MEC contaminated sites shall be familiar with the potential safety and health hazards associated with the conduct of demolition/disposal operations, and with the work practices and control techniques used to reduce or eliminate these hazards. During demolition operations, general safety provisions listed below will strictly followed by all demolition personnel. Non-compliance with the general safety provisions will result in disciplinary action, to include termination of employment if warranted.

- All safety regulations applicable to demolition range activities and the destruction of MEC materials involved shall be complied with.

- Demolition of any kind is prohibited without the express permission from the client.

- The quantity of MEC to be destroyed will be determined by the range limit, with the Net explosive weight (NEW) of the demolition explosives factored into the total NEW.

- In the event of an electrical storm, or heavy snow or dust storms, immediate action will be taken to cease all demolition range operations and evacuate the area.

- In the event of a fire or unplanned explosion, if possible, put out the fire. If unable to do so, notify fire and police departments and evacuate the area. If injuries are involved, remove victims from danger, administer first aid and seek medical attention.

- The DS is responsible for reporting all injuries and accidents that occur to the UXOSO.

- Demolition team personnel will not tamper with any safety devices or protective equipment.

- Any defect in demolition material or an unusual condition that is not covered by this SOP will be reported immediately to the DS and UXOSO.

- Demolition procedures shall be conducted in accordance with this SOP and applicable references in section 3.0.

- Adequate fire protection and first aid equipment shall be provided at all times.

- All personnel engaged in the destruction of MEC shall wear under and outer garments made of close-weave natural fiber, such as cotton. Synthetic material such as nylon is not authorized unless treated with anti-static material.

- Care will be taken to minimize exposure to the smallest number of personnel, for the shortest time, to the least amount of hazard, consistent with safe and efficient operations.

- Work locations will be maintained in a neat and orderly condition.

- All demolition hand tools shall be maintained in a good state of repair.

- Each heavy equipment and/or vehicle operator will have in his possession a valid operator's permit, i.e., state driver’s license, certificate of training for backhoe/excavator etc.

- Leather or leather-palmed gloves will be worn when handling wooden boxes, munitions or MEC. If bulk or binary explosives are being handled then rubber gloves, such as Nitrile, will be worn

- Lifting and carrying require care. Improper methods cause unnecessary strains. Observe the following preliminaries before attempting to lift or carry:
  - When lifting, keep your arms and back as straight as possible, bend your knees and lift with your leg muscles; and
  - Be sure you have good footing and hold, and lift with a smooth, even motion.
- The demolition range shall be provided with telephone and/or radio communication.
- Motor vehicles and material handling equipment (MHE) used for transporting MEC or demolition materials must meet the following requirements:
  - Exhaust systems shall be kept in good mechanical repair.
  - Lighting systems shall be an integral part of the vehicle.
  - One 20 BC rated portable fire extinguisher shall be, if possible, mounted on the vehicle outside of the driver's cab or two 10BC fire extinguishers, with one inside the cab and the other near the front portion of the vehicle bed, nearest the driver.
  - Wheels of carriers must be chocked and brakes set during loading and unloading.
  - No demolition material or MEC shall be loaded into or unloaded from, motor vehicles while the engine is operating.
- Motor vehicles and MHE used to transport demolition material and MEC shall be inspected prior to use to determine that:
  - Fire extinguishers are filled and in good working order.
  - Electrical wiring is in good condition and properly attached.
  - Fuel tank and piping are secure and not leaking.
  - Brakes, steering and safety equipment are in good condition.
  - The exhaust system is not exposed to accumulations of grease, oil, gasoline, or other fuels, and has ample clearance from fuel lines and other combustible materials.
- A red warning flag, such as a "Bravo Flag", a windsock, or rag will be displayed at the entrance to the demolition range and, if applicable, the entrance gate shall be locked when demolition work is in process. This is only applicable if an open detonation (OD) range has been established with demo pits for all shots.
- Unless otherwise directed, all demolition shots will be tamped with a minimum of two feet of clean earth/dirt.

- An observer will be stationed at a location where there is a good view of the air and surface approaches to the demolition range before material is detonated. It shall be the responsibility of the observer to order the DS to suspend firing if any aircraft, vehicles or personnel are sighted approaching the general demolition area.

- Two-way radios shall not be operated on the demolition range while the shot is primed or during the priming process. The charts shown in Attachment 1 of this SOP shall be used for determining the safe distances from transmitter antennas.

- No Demolition operation will be left unattended during the active portion of the operation (i.e., during the burn or once any explosives or MEC are brought to the range).

- A minimum area of 200 feet in diameter shall be cleared of dry grass, leaves and other extraneous combustible materials around the demolition shot/pit area.

- No demolition activities will be conducted if there is less than a 2,000-foot ceiling or if wind velocity is in excess of 20 mph.

- Demolition-shots must be fired during daylight hours (i.e., between 30 minutes after sunrise and 30 minutes before sunset).

- No more than two persons shall ride in a truck transporting demolition material or MEC, and no person shall be allowed to ride in the trailer/bed.

- Vehicles shall not be refueled when carrying demolition material or MEC, and must be 100 feet from magazines or trailers containing such items before refueling.

- All explosive vehicles will be cleaned of visible explosive and other contamination before releasing the vehicles for other tasks.

- Prior to conducting any other task, personnel shall wash their face and hands after handling demolition material or MEC.

- At the demolition site, prior to “check-out” procedures, all blasting caps will be stored in approved containers and separated a minimum of 50 feet “downwind” from all other explosives until they are needed.

- Demolition shots/pits shall be spaced at least 50 feet apart, with no more than 10 shots/pits prepared for a series of shots at any one time.

6.0 SPECIAL REQUIREMENTS FOR DEMOLITION ACTIVITIES

The following safety and operational requirements shall be followed during demolition range operations. Any deviations from this procedure shall be allowed only after receipt of

written approval from the PM and the UCACE. Failure to adhere to the requirements and procedures listed in the paragraphs below could result in serious injury or death; therefore complete compliance with these requirements and procedures will be strictly enforced.

6.1 General Requirements

The general demolition range/shot requirements listed below shall be followed at all times:

- Attachment 1 of this SOP, Explosive Hazards Tables, will be adhered to in all demolition operations.

- Attachment 2 of this SOP, "Procedures for Demolition of Multiple Rounds (Consolidated Shots) on Ordnance and Explosives (OE) Sites," will be followed when destroying multiple munitions by detonation.

- Attachment 3 of this SOP, “Use of Water for Mitigation of Fragmentation and Blast Effects Due to Intentional Detonation of Munitions” may be used when fragmentation throws and fire is a concern.

- Material awaiting destruction shall be stored at not less than intra-line distance, based on the largest quantity involved, from adjacent explosive materials and from explosives being destroyed. The material shall be protected against accidental ignition or explosion from fragments, grass fires, burning embers or detonating impulses originating in materials being destroyed.

- MEC or bulk explosives, acceptable to move, and destroyed by detonation can be detonated in a pit not less than three feet deep and covered with earth which protrudes not less than two feet above existing ground level. The components should be placed on their sides or in a position to expose the largest area to the influence of the demolition material. The demolition material should be placed in intimate contact with the item to be detonated and held in place by tape or earth packed over the demolition materials. The total NEW to be destroyed below ground at one time shall not exceed the range limit.

- Prevailing weather condition information will be obtained from the U.S. Weather Service and the data logged in the Demolition Shot Log before each shot or round of shots.

- All shots shall be dual primed.

- A minimum of 30 seconds will be maintained between each detonation.

- Detonations will be counted to ensure detonation of all shots. After each series of detonations, a search shall be made of the surrounding area for unexploded MEC. Items such as lumps of explosives or unfuzed ammunition may be picked up and prepared for the next shot. Fuzed ammunition or items that may have internally damaged components will be detonated in place, if possible.

- After each-detonation and at the end of each day's operations, surface exposed munitions debris, shall be recovered from the demolition range and disposed of in accordance with contracted procedures, as well as all applicable environmental regulations. All collected munitions debris metal will be 100% inspected for absence of explosive materials by demolition range personnel and certified by the SUXOS and the UXOQCS.

- When operated in accordance with the conditions of this procedure the demolition range/shot should not present a noise problem to the surrounding community. However, if a noise complaint is received, the name, address and phone number of the complainant should be recorded and reported to the site manager, who report it to the USACE.

- Whenever possible, during excavation of demolition pits contour the ground so that runoff water is channeled away from the pits. If demolition operations are discontinued for more than two weeks, the pits should be back filled until operations resume.

- Upon completion of the project, all disturbed demolition areas will be thoroughly inspected for MEC. According to the SOW, the site may have to be leveled and seeded to establish a permanent vegetative cover to inhibit erosion. If necessary, this will be coordinated with the contractor representative. At a minimum, the holes/pits will be filled in and contoured.

- Prior to and after each shot, the Demolition Shot Record is to be filled out by the DS with all applicable information.

6.2 Electric Detonator Use

The following requirements are necessary when using electric detonators and blasting circuits:

- Electric detonators and electric blasting circuits may be energized to dangerous levels from outside sources such as static electricity, induced electric currents and radio transmission equipment. Safety precautions will be taken to reduce the possibility of a premature detonation of an electric detonator and explosive charges of which they form a part. Demolition Team radios will not be operated while the pit/shot is primed or during the priming process.

- Demolition team members handling detonators will first ground themselves by bending down and touching the ground, which will discharge any static electricity.

- The shunt shall not be removed from the leg wires of the detonator until the continuity check.

- When uncoiling or straightening the detonator leg wires; keep the explosive ends of the detonator pointing away from the body and away from other personnel. When straightening the leg wires, do not hold the detonator itself; rather hold the detonator leg wires approximately one inch from the detonator body. Straighten the leg wires by hand, do not throw or wave the wires through the air to loosen them.

- Prior to use, the detonators shall be tested for continuity. To conduct the test, place the detonators in a pre-bored hole in the ground or place them in a sand bag and walk facing away from the detonators and stretch the wires to their full length, or to 25 feet, whichever is less, being sure to not pull the detonators from the hole or sand bag. With the leg wires stretched to their full length, test the continuity of the detonators one at a time by un-shunting the leg wires and attaching them to the galvanometer and checking for continuity. After the test, re-shunt the wires by twisting the two ends together. Repeat this process for each detonator until all detonators have been tested. This process shall be accomplished at least 50 feet down wind from any MEC/demolition materials and out of the personnel and vehicle flow patterns. In addition, all personnel on the demolition range/shot shall be alerted prior to the test being conducted.

  NOTE: When testing the detonator, prior to connecting the detonator to the firing circuit, the leg wires of the detonator must be shunted by twisting the bare ends of the wires together immediately after testing. The wires shall remain short circuited until time to connect them to the firing line.

- At the power source end of the blasting circuit, the ends of the firing line wires shall be shorted or twisted together (shunted) at all times, except when actually testing the circuit or firing the charge. The connection between the detonator and the circuit firing wires must not be made unless the power end of the firing wires are shorted and grounded or the firing panel is off and locked.

- The firing line will be checked using pre-arranged hand signals or through the use of two-way radios if the demolition pit/shot is not visible from the firing point. If radios are used, communication shall be accomplished a minimum of 50 feet from the demolition pit/shot and detonators. The firing line will be checked for electrical continuity in both the open and closed positions, and will be closed and shunted prior to connecting the detonator leg wires.

- MEC to be detonated or vented shall be placed in the demolition pit/shot and the demolition material placed/attached in such a manner as to ensure the total detonation and/or venting of the MEC. A section of detonation cord, time fuze, or Non-El shock tube will extend from the demolition material to a point outside the tamping material. Once the MEC and demolition material are in place and the shot has been tamped, the detonators will be connected to the demolition material. Prior to handling detonators that are connected to the firing line, personnel shall ensure that they 0nce again ground themselves. The detonators will then be carried to the demolition pit/shot with the end

of the detonators pointed away from the individual. The detonators are then connected to the detonation cord, Non-El, etc., ensuring that the detonator is not covered with tamping material to allow for ease of recovery/investigation in the event of a miss-fire.

- Prior to making connections to the blasting machine, the entire firing circuit shall be tested with a galvanometer for electrical continuity and ohmic resistance to ensure the blasting machine has the capacity to initiate the shot.

- The individual assigned to make the connections at the blasting machine or panel will not complete the circuit at the blasting machine or panel and will not give the signal for detonation until satisfied that all personnel in the vicinity have been evacuated to a pre-determined distance as computed by CEHNC-ED-CS-S or the default distance found in DoD 6055.9-STD. When in use, the blasting machine or its actuating device shall be in the blaster's possession at all times. When using the panel, the switch must be locked in the open position until ready to fire, and the single key must be in the blaster's possession.

- Prior to initiating a demolition shot(s), a warning will be given, the type and duration of such will be determined by the prevailing conditions at the demolition range/shot. At a minimum, this should be an audible signal using a siren, air horn or megaphone, which is sounded for one minute duration, five minutes prior to the shot and again one minute prior to the shot.

6.3 Detonating Cord Use

The following procedures are required when using detonating cord (det cord):

- Det cord should be cut using approved crimpers and only the amount required should be removed from inventory.

- When cutting det cord, the task should be performed outside the magazine.

- For ease of inventory control, only remove det cord in one-foot increments.

- Det cord should not be placed in clothing pockets or around the neck, arm or waist, and should be transported to the demolition location in either an approved "day box" or a cloth satchel, depending upon the magazine location and proximity to the demolition area.

- When ready to "tie in" either the det cord to demolition materials, or det cord to detonator, the det cord will be connected to the demolition material and secured to the MEC. The cord is then strung out of the hole/tamping material and secured in place with soil, being sure to leave a one-foot tail exposed outside the hole/tamping material.

- Once the hole is filled or tamping in place, make a loop in the det cord large enough to accommodate the detonator, place the detonator in the loop and secure it with tape. The detonator's explosive end will face down the det cord toward the demolition material or parallel to the main line.

- In all cases, ensure there is sufficient det cord extending out of the hole/tamping material to allow for ease of detonator attachment and detonator inspection/replacement should a misfire occur.

- If the det cord detonators are electric, they will be checked, tied in to the firing line and shunted prior to being taped to the loop as described above. If the det cord detonators are non-electric, the time/safety fuse will be prepared with the igniter in place prior to taping the detonators to the det cord loop. If the det cord detonators are Non-El, simply tape the detonators into the loop as described above.

- In the event that a time/safety fuse is used, and an igniter is not available and a field expedient initiation system must be used (i.e., matches), do not split the safety fuse until the detonator is taped into the det cord loop.

6.4 Shock Tube Splicing Procedures

The high reliability of the shock tube initiating system is due to the fact that all of the components are sealed and unlike standard non-electric priming components, cannot be easily degraded by moisture. Cutting the shock tube makes the open end vulnerable to moisture and foreign contamination, therefore care must be taken to prevent moisture and foreign matter from getting in the shock tubes exposed ends. Some general rules to follow are listed below.

- After cutting a piece of shock tube, either immediately tie a tight overhand knot in one or both cut ends or splice one exposed end and tie off the other.

- Always use a sharp knife or razor blade to cut shock tube so as to prevent the tube from being pinched or otherwise obstructed.

- Always cut shock tube squarely across and make sure the cut is clean.

- Use only the splicing tubes provided by the manufacturer to make splices

- Every splice in the shock tube reduces the reliability of the priming system; therefore keep the number of splices to a minimum.

6.4.1 Shock Tube Assembly

Step 1. If you are using a new role of shock tube cut off the sealed end, dispose of the small piece IAW local laws as they relate to flammable material and proceed to the directions listed in Step 3. If you are using a pre-assembled shock tube/detonator assembly proceed to Step 1 in paragraph 6.4.2.

Step 2. If you are using a previously cut piece of shock tube, using a sharp knife or razor blade cut approximately 18 inches from the previously cut end, whether or not it was knotted IAW the above guidance. Dispose of the 18-inch piece of shock tube IAW local regulations.

Step 3. Using a sharp knife or razor cut the sealed end off of the detonator assembly and dispose of the small piece as above.

Step 4. Loosely tie the two shock tube ends to be sliced together in a square knot, leaving at least a two-inch free end of each end of the shock tube beyond the knot. Push the shock tube lightly to tighten the knot, but not so tight as to significantly deform the shock tube.

Step 5. Push one of the shock tube ends to be spliced firmly into one of the precut splicing tubes provided by the manufacturer, at least ¼ inches. Push the other shock tube end firmly into the other end of the splicing tube at least ¼ inches.

Step 6. Spool out the desired length of shock tube and cut it off with a sharp knife or razor blade.

Step 7. Immediately seal off the shock tube remaining on the spool by tying a tight overhand knot in the cut off end.

6.4.2 Firing Assembly Setup

Step 1. Lay out the required length of shock tube from demo area to firing point.

Step 2. If there are multiple items to be destroyed using bunch block(s), supplied by the manufacturer, lay out lead lines at demo site to the shot(s) and secure the bunch block with a sandbag, or some other item which will keep it from moving. Figure 1 illustrates the procedure.

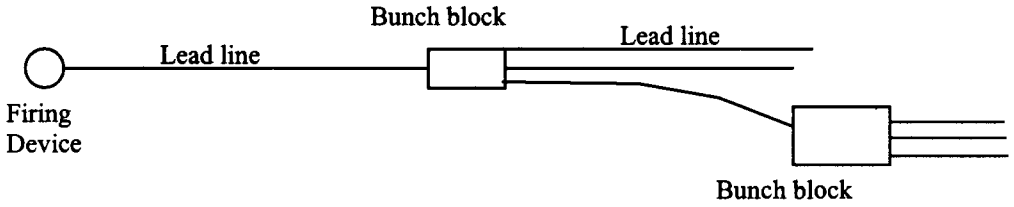


Figure 1

Note: No more than six leads may be used from any one bunch block.

Step 3. If the detonator assembly has not been attached yet then using the splicing tube, splice the detonator assembly to the shock tube lead line as explained in the splicing instructions above.

Step 4. If this is a non-tamped shot place the detonator assembly into the demolition material. If the shot is to be tamped then prepare the demolition material with a detonating cord lead long enough to stick out of the tamping at least one foot.

Step 5. Tape the detonator assembly to the detonating cord lead as shown in Figure 2.

Step 6. Clear the area IAW the approved demolition plan, return to the firing position.

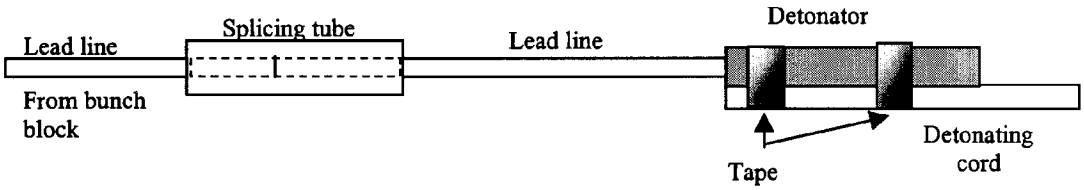


Figure 2

Step 7. Insert a primer into the firing device and connect the shock tube lead line to the firing device ensuring that the shock tube is properly seated in the firing device.

Step 8. Proceed IAW the approved demolition procedures.

6.5 Time/Safety Fuse Use

The following procedures are required when using a time/safety fuse:

- Prior to each daily use, the burn rate for the time/safety fuse must be tested to ensure the accurate determination of the length of time/safety fuse needed to achieve the minimum burn time of five minutes needed to conduct demolition operations.
- To ensure both ends of the time/safety fuse are moisture free, use approved crimpers to cut six inches off the end of the time/safety fuse roll and place the six inch piece in the time/safety fuse container.
- If quantity allows, accurately measure and cut off a six foot long piece of the time/safety fuse from the roll, and take the six-foot section out of the magazine and attach a fuse igniter.
- In a safe location, removed from demolition materials and MEC, ignite the time/safety fuse, measure the burn time from the point of initiation to the "spit" at the end, and record the burn time in the DS's Log.
- To measure the burn time, use a watch with a second hand, stop watch or chronograph.
- To calculate the burn rate in seconds per foot, divide the total burn time (in seconds) by the length (in feet) of the test fuse.
- Whenever using time/safety fuse, for demolition operations, the minimum amount of fuse to be used will be the amount needed to permit a minimum burn time of five minutes.

6.6 Perforator Use

The following procedures are required when using perforators:

- Only remove from inventory the number of perforators required to perform the task.

- Transport perforators in an approved "day box", cloth satchel or plastic container, depending upon magazine location and proximity to the demolition operations.

- When ready to use, place the det cord through the slot on the perforator and knot the det cord, ensuring the cord fits securely and has good continuity with the perforator.

- Once the det cord is secure, place the perforator in the desired location and secure it in place.

- Proceed from this point as described in paragraph 6.3.

6.7 Use of Two-Component Explosives

The following procedures are required when using two-component (binary) demolition materials:

- Only remove from inventory the amount of two-component required to perform the task.

- When transporting the solid and liquid, they need only be placed apart in the bed of a truck.

- Do not mix the solid and liquid components until certain that it will be used, since the resulting mixture is classified as a Class 1.1 explosive by Department of Transportation.

- When mixing the solid and liquids components, follow the manufacturer's instructions, while being sure to wear rubber gloves and goggles. Mix components in an area away from other demolition materials, the MEC, and if possible, sheltered from the wind.

- Once the components have been mixed, it is essential that the lid to the solid bottle be put on securely as soon as possible after mixing to prevent evaporation of the liquid.

- Attach the det cord as recommended by the manufacturer, place the assembled unit in the desired location in the hole/shot and secure the unit.

- Proceed from this point as described in paragraph 6.3.

6.8 Demolition Range/Shot Inspection Schedule

The demolition range inspection schedule outlined in Table 6-1 will be followed at all sites where demolition operations are being conducted. This inspection shall be conducted by the UXOSO and will be documented in the Site Safety Log. If any deficiencies are noted, demolition operations shall be suspended and the deficiency reported to the SUXOS and DS. Once the deficiencies are corrected, demolition operations may be resumed.

Table 6-1 - Demolition Range Inspection Schedule

Check List Item	Inspection Schedule	Check List Item	Inspection Schedule
Site and Explosive Carrier Vehicle	Weekly or Prior to Use	Personal Protective Equipment	Prior to Use
Range Access/Egress Route	Weekly or Prior to Use	Circuit Testing Device	Prior to Use
Entrance Gate/Lock	Weekly or Prior to Use	Demolition Site	Prior to Use
Storage Trailer/Magazine	Daily, Prior to Use and After Use	Operating Equipment	Prior to Use
Fire Extinguishers	Daily, Prior to Use and After Use	Hospital Route	Prior to Use

7.0 METEOROLOGICAL CONDITIONS

In order to control the effects of demolition operations and to ensure the safety of site personnel, the following meteorological limitations and requirements shall apply to demolition operations:

- Demolition operations will not be conducted during electrical storms or thunderstorms.
- No demolition operations shall be conducted if the surface wind speed is greater than 20 miles per hour.
- Demolition operations will not be conducted during periods when visibility is less than one mile caused by, but not limited to, dense fog, blowing snow, rain, sand or dust storms.
- Demolition shall not be carried out on extremely cloudy days that are defined as: overcast (more than 80% cloud cover) with a ceiling of less than 2,000 feet.
- Demolition operations will not be conducted during any atmospheric inversion condition (low or high altitude).
- Demolition operations will not be conducted during periods of local air quality advisories.
- Demolition operations will not be initiated until 30 minutes after sunrise, and will be secured at least 30 minutes prior to sunset.

8.0 PRE-DEMOLITION/DISPOSAL PROCEDURES

8.1 Pre-Demo/Disposal Operational Briefing

It is the belief of Parsons that the success of any operation is dependent upon a thorough brief, covering all phases of the task, which is presented to all affected personnel. The DS will brief all personnel involved in range/shot operations in the following areas:

- Type of MEC being destroyed.
- Type, placement and quantity of demolition material being used.
- Method of initiation (electric, non-electric or Non-El).
- Means of transporting and packaging MEC, if applicable.
- Route to the disposal site.
- Emergency procedures.
- Equipment being used (i.e., galvanometer, blasting machine, firing wire, etc.).
- Misfire procedures.
- Post shot clean up of range.

8.2 Pre-Demo/Disposal Safety Briefing

The UXOSO and DS will conduct a safety brief for all personnel involved in range operations in the following areas:

- Care and handling of explosive materials.
- Personal hygiene.
- Two-man rule and approved exceptions.
- Potential trip/fall hazards.
- Horseplay on the range.
- Stay alert for any explosive hazards.
- Location of emergency shelter (if available).
- Vehicle parking (vehicles must be oriented out of the site for immediate departure, with keys in the ignition).
- Location of emergency vehicle (keep engine running).
- Wind direction (to assess potential toxic fumes).
- Location of first aid kit and fire extinguisher.
- Route to nearest hospital or emergency aid station.
- Type of communications in event of an emergency.
- Storage location of demolition materials and MEC awaiting disposal.

8.3 Task Assignments

Individuals with assigned tasks will report the completion of the task to the DS. The types of tasks that may be required are:

- Contact local Police, Fire department, USCG and FAA as required.
- Contact hospital/emergency response personnel if applicable.
- Secure all access roads to the range/shot area.

- Visually check range/shot area for any unauthorized personnel.
- Check firing wire for continuity and shunt.
- Prepare designated pits/shots as required.
- Check continuity of detonators.
- Check time/safety fuse and its burn rate.
- Designate a custodian of the blasting machine, fuse igniters or Non-El initiator.
- Secure detonators in a safe location.
- Place MEC in pit, if applicable, and place charge in desired location.

8.4 Preparing Explosive Charge for Initiation

To prepare the explosive charge for initiation, the procedures listed below will be followed:

- Ensure firing wire is shunted.
- Connect detonator to the firing wire.
- Isolate or insulate all connections.
- Prime the demolition charge.
- Place demolition charge on MEC.
- Depart to firing point (if using non electric firing system, obtain head count, pull igniters and depart to designated safe area).
- Obtain a head count, and test blast machine for proper operation.
- Give one-minute duration warning signal, using a bullhorn or siren, five minutes prior to detonation, and again at one minute prior to detonation.
- Check the firing circuit with a galvanometer.
- Yell **"fire in the hole"** three times (or an equivalent warning) and take cover.
- If using electric firing system connect firing wires to blasting machine and initiate charge.
- Remove firing wires from blasting machine and shunt.
- Remain in designated safe area until DS announces **"All Clear"**. This will occur after a post-shot waiting period of 5-minutes and the UXOSO has and inspected the pit(s)/shot(s).

9.0 POST DEMOLITION/DISPOSAL PROCEDURES

Do not approach a smoking hole or allow personnel out of the designated safe area until cleared to do so, and follow the below listed procedures:

- After the **"All Clear"** signal, check pit/shot for low orders or kick outs.
- Check pit with a magnetometer and remove any large fragmentation.
- Any MEC items, failing to be properly disposed of, discovered during the post demolition procedures, will be destroyed prior to the end of the day.
- Back fill hole as necessary.
- Police up all equipment.
- Notify police, fire, etc. that the operation is complete.

10.0 MISFIRE PROCEDURES

A thorough check of all equipment, firing wire and detonators will prevent most misfires. However, if a misfire does occur, the procedures outlined below shall be followed.

10.1 Electric Misfires

To prevent electric misfires, one technician will be responsible for all electrical wiring in the circuit. If a misfire does occur, it must be cleared with extreme caution, and the responsible technician will investigate and correct the situation, using the steps outlined below:

- Check firing line and blasting machine connections and make a second initiation attempt.
- If unsuccessful, disconnect and connect to another blasting machine (if available) and attempt to initiate charge.
- If unsuccessful, commence a 60-minute wait period.
- After the maximum delay predicted for any part of the shot has passed, the UXOSO will proceed down range to inspect the firing system, and a safety observer must watch from a protected area.
- Disconnect and shunt the detonator wires from the leg wires, connect a new detonator to the firing circuit, check the replacement detonator for continuity, and prime the charge without disturbing the original detonator.
- Follow normal procedures for effecting initiation of the charge.

10.2 Non-Electric Misfires

Working on a non-electric misfire is the most hazardous of all operations. Occasionally, despite all painstaking efforts, a misfire will occur. Investigation and corrective action should be undertaken only by the technician that placed the charge, using the following procedure:

- If charge fails to detonate at the determined time, initiate a 60-minute wait period plus the time of the safety fuse, i.e., 5-minute safety fuse plus 60 minutes for a total of 65 minutes.
- After the wait period has expired, the designated technician will proceed down range to inspect the firing system. A safety observer must watch from a protected area.
- Prime the shot with a new non-electric firing system and install a new fuse igniter.
- Follow normal procedures for initiation of the charge.

10.3 Non-EL Misfire

The most common cause of misfires is known as "black tube failure". The shock tube propagates up to the detonator but the detonator fails to function, or there is a crimp in the line

causing the shock wave to be interrupted. The following steps will be taken in the event of a misfire:

- If the shock tube fails to propagate and the tube remains clear, remove the shock tube from the firing device, cut off six inches of the shock tube, insert a new primer, re-insert the shock tube ensuring that it is properly seated and re-fire. If when you activate the firing device and the shock tube gets blown out of the firing device without activating, cut off six inches of the shock tube, replace the primer and re-insert the shock tube into the firing device.

- If the primer functioned properly and the shock tube was heard or seen to fire, observe the standard one-hour waiting period prior to going downrange.

- After the one-hour waiting period has passed, proceed downrange and check the first component in the priming train i.e. splice, bunch block or detonator assembly. Repeat this process till you reach the detonator assembly. As you conduct this inspection and discover the problem, replace the firing train, which functioned (tube is no longer clear) with a new one and ensure that all the connections are correct and secure.

- After the system has been checked and repaired/replaced return to the firing point and repeat the firing process.

10.4 Detonating Cord Misfire

Parsons uses det cord to tie in multiple demolition shots and to ensure that electric detonators are not buried. Since det cord initiation will be either electrical or non-electrical, the procedures presented in paragraphs 10.1, 10.2, or 10.3, as appropriate to the type of detonator used, will be used to clear a det cord misfire. In addition, the following will be followed:

- If there is no problem with the initiating system, wait the prescribed amount of time and inspect the initiator to the cord connection to ensure it is properly connected. If it was a bad connection simply attach a new initiator and follow the appropriate procedures in paragraph 6.0.

- If the initiator detonated and the cord did not, inspect the cord to ensure it is det cord and not time fuze. Also, check to ensure there is PETN in the cord at the connection to the initiator.

- It may be necessary to uncover the det cord and replace it. This must be accomplished carefully to ensure that the demolition charge and the MEC item are not disturbed.

10.5 Perforator Misfire

The use of perforators is considerably safer than the use of C-4 and many other demolition materials. If the perforator is not initiated properly, it could malfunction. Since the perforator is covered with tamping material, det cord is used as the initiator. Therefore, in the event of a misfire, the procedures presented in paragraph 10.4 will be followed, along with the items presented below:

- If everything went but the perforator, one of four things has occurred:

    1. Det cord grain size was insufficient to initiate the perforator;

- Check to ensure the grain size of the det cord is sufficient, with 80-grain size or greater being the recommended size.

    2. The det cord was dislodged from the perforator when placing tamping materials;

- If the det cord connection to the perforator was the problem, ensure that the next connection is secured (use duct tape if necessary).

    3. The perforator was defective;

    4. The perforator was moved during the placement of tamping materials.

- If it is evident that the perforator was moved, ensure it is properly secured for the next shot.

- If cord size and connection are sufficient, replace the perforator, leaving the defective one on the shot.

11.0 RECORD KEEPING REQUIREMENT

To document demolition operations and the destruction of MEC, the following record keeping requirements shall be met:

- Parsons and/or its subcontractors will obtain and maintain all required permits.

- The DS will ensure the accurate completion of the logs, and the SUXOS and UXOQCS will monitor the entries in the log for completeness, accuracy and compliance with meteorological conditions.

- The DS shall enter the appropriate data on the Demolition Shot Record, to reflect the MEC destroyed, and shall complete the appropriate information on the Magazine Data Card, which indicates the demolition materials used.

- The quantities of MEC recovered must also be the quantities of MEC destroyed or disposed of as munitions debris or munitions constituents.

- Parsons and/or its subcontractors will retain a permanent file of all Demolition Records, including permits, Magazine Data Cards, training records, inspector reports, waste manifests if applicable, and operating logs.

- Copies of ATF License and any state or local permits must be on hand.

12.0 SAFETY AND PPE REQUIREMENTS

The following safety measures and personal protective equipment shall be used in preventing or reducing exposure to the hazards associated with MEC demolition/disposal operations. These requirements will be implemented unless superseded by site specific requirements stated in the Accident Prevention Plan (APP):

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1. Steel-toed safety boots will not be worn by demolition team personnel conducting demolition/disposal operations, unless a toe crush hazard exists, in which case personnel will wear boots with plastic or fiber toed safety toes;

2. Unless a serious head, eye or face hazard exists, demolition team personnel will not be required to wear hard hats, safety glasses or face shields when conducting operations involving the handling of demolition explosives or MEC, except as stated previously; and

3. In the event that a serious head, eye or face hazard does exist, demolition team personnel will wear the required PPE, but positive restraining means shall be required to secure the PPE to the head, face etc. and prevent it from falling and causing an accidental detonation.

13.0 AUDIT CRITERIA

The following items related to demolition/disposal operations on an MEC contaminated site will be audited to ensure compliance with this SOP:

1. The Demolition Shot Record
2. The Site Daily Operational and Safety Logs;
3. The MEC Operations Daily/Weekly Report;
4. The Safety Training Attendance Forms, for the initial site hazard training;
5. The Safety Training Attendance Forms, for the Daily Tailgate Safety Briefings;
6. The Daily Safety Inspection and Audit Log.

14.0 ATTACHMENTS

The following attachment to this SOP will be reviewed by all UXO-qualified personnel participating in demolition/disposal activities.

- Attachment l Explosive Hazards Tables

- Attachment 2 "Procedures for Demolition of Multiple Rounds Consolidated Shots on Ordnance and Explosives (OE) Sites"

- Attachment 3 Use of Sandbags for Mitigation of Fragmentation and Blasts Effects due to Intentional Detonation of Munitions (HNC-ED-CS-S-98-7)

- Attachment 4 Use of Water for Mitigation of Fragmentation and Blasts Effects due to Intentional Detonation of Munitions (HNC-ED-CS-S-00-3)

- Attachment 5 Weapon Specific Fragmentation Characterization (DDESB TP 16)

ATTACHMENT 1

EXPLOSIVE HAZARDS TABLES

INTRODUCTION

The following tables are to be used during demolition operations, and will be used to calculate minimum safe distances as they relate to mobile RF, television and FM broadcasting transmitters.
Tables 1-1 and 1-2 are to be used for determining the minimum safe distances to be maintained from different types of radio and television transmitters when electric detonators are in use.

Table 1-1 – Minimum Safe Distance from Transmitter Antennas

Average or Peak Transmitter Power in Watts	**Minimum Distance to Transmitter in Feet /Meters**
0 –30	30 / 98.4
31 – 50	50 / 164.1
51 – 100	110 / 360
101 – 250	160 / 525
251 – 500	230 / 755
501 – 1,000	305 / 1,000
1,001 – 3,000	480 / 1,575
3,001 – 5,000	610 / 2,001
5,001 – 20,000	915 / 3,002
20,001 – 50,000	1,530 / 5,020
50,001 – 100,000	3,050 / 10,007
100,001 – 400,000	6,100 / 20,014
400,001 – 1,600,000	12,200 / 40,028
1,600,001 – 6,400,000	24,400 / 80,056
Note: When the transmission is a pulsed or pulsed continuous wave type and its pulse width is less than 10 microseconds, the power column indicates average power. For all other transmissions, including those with pulse widths greater than 10 microseconds, the power column indicates peak power.	

Source: DA PAM 385-64, Table 6-3.

Table 1-2 – Safe Separation Distance Equations

	Un-Sheilded Munitions		Sheilded Munitions	
	Frequency	Formula	Frequency	Formula
	≤2.3 KHz	$D = 0.093 \times (PG)^{0.5}$	≤73 KHz	$D = 0.093 \times (PG)^{0.5}$
	2.3 KHz – 0.45 MHz	$D = 39.7 \times F \times (PG)^{0.5}$	73 KHz – 0.45 MHz	$D = 126 \times F \times (PG)^{0.5}$
	0.45 MHz – 400 MHz	$D = 18 \times (PG)^{0.5}$	0.45 MHz – 400 MHz	$D = 0.6 \times (PG)^{0.5}$
	400 MHz – 75 GHz	$D = (7137 / F) \times (PG)^{0.5}$	400 MHz – 2.4 GHz	$D = (226 / F) \times (PG)^{0.5}$
	>75 GHz	$D = 0.093 \times (PG)^{0.5}$	>2.4 GHz	$D = 0.093 \times (PG)^{0.5}$

Where:

D = Safe distance to the transmitter in feet (multiply feet by 0.305 to obtain meters)
P = Output power of the transmitter in watts
G = Numerical gain of transmitter antenna
F = Frequency in MHz (divide KHz by 1,000 to obtain MHz, and multiply GHz by 1,000 to obtain MHz)

To properly use this table, the following assumptions are made:

1. NO-FIRE CURRENT = 10 mA.
2. SAFETY FACTOR = 10 dB or 3.16 numerical).
3. EED'S LEADS = Tuned to match the transmitter's frequency.
4. SHEILDING = If metallic, it provides a minimum of 30 dB or 32 times (numerical) of shielding. Non-metal packs provide no shielding.
5. At no time should personnel or munitions be exposed to more than 200 volts/ meter (rms).

Source: DA PAM 385-64, Table 6-4.

ATTACHMENT 2

PROCEDURES FOR DEMOLITION OF MULTIPLE ROUNDS (CONSOLIDATED SHOTS) ON ORDNANCE AND OE SITES

US Army Corps of Engineers
Engineering and Support Center, Huntsville

Procedures for Demolition of Multiple Rounds (Consolidated Shots) on Ordnance and Explosives (OE) Sites

AUGUST 1998 (Terminology Update March 2000)

DEPARTMENT OF DEFENSE EXPLOSIVES SAFETY BOARD
2461 EISENHOWER AVENUE
ALEXANDRIA, VIRGINIA 22331-0600

OCT 27 1998

DDESB-KO

MEMORANDUM FOR DIRECTOR US ARMY TECHNICAL CENTER FOR EXPLOSIVES SAFETY (ATTENTION: SIOAC-ES)

SUBJECT: Procedures for Demolition of Multiple Rounds (Consolidated Shots) on Ordnance and Explosives Sites

References: (a) Memorandum from SIOAC-ESL to Chairman DDESB (ATTN: DDESB-KO), 14 September 1998, SAB

(b) M. Crull and Wayne Shaw, US Army Corps of Engineers, Huntsville, "Procedures for Demolition of Multiple Rounds (Consolidated Shots) on Ordnance and Explosives (OE) Sites" (August 1998)

The subject procedures forwarded by reference (a) and defined in reference (b) have been reviewed with respect to explosives safety criteria. Based on the information furnished, the procedures proposed in reference (b) for the demolition of consolidated ordnance at OE sites are approved.

Point of contact is Dr. Chester E. Canada, DDESB-KT2 (PH: 703-325-1369, FAX: 703-325-6227, E-MAIL: canadce@hqda.army.mil).

for DANIEL T. TOMPKINS
Colonel, USAF
Chairman

Procedures for Demolition of Multiple Rounds (Consolidated Shots) on Ordnance and Explosives (OE) Sites

August 1998

Prepared By

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Reviewed by: _____ 8/27/98
Chief, Structural Branch — Date

Reviewed by: _____ 8/27/98
Chief, Civil-Structures Division — Date

Reviewed by: _____ 8/27/98
Chief, OE Center of Expertise — Date

Reviewed by: _____ 8/31/98
Chief, Ordnance & Explosives Team — Date

Reviewed by: _____ 8/31/98
Chief, OE Safety — Date

FOREWORD

The terminology in this report has been updated (March 2000) to reflect terminology used in the field. Specifically the term “personnel separation distance” has been replaced with the term “minimum separation distance for intentional detonations.” This is a change in terminology only, no change in content.

Per discussions with Dr. Chester Canada, Department of Defense Explosives Safety Board (DDESB) and Mr. Cliff Doyle, U.S. Army Technical Center for Explosives Safety (USATCES) this report is not re-submitted to the DDESB for approval.

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LIST OF FIGURES

1.0 Introduction

The U.S. Army Engineering and Support Center, Huntsville (USAESCH) includes the Ordnance and Explosives Center of Expertise (OE-CX). Part of the OE-CX mission is development of procedures for removal and destruction of munitions found on OE sites. Standard procedures are to destroy the munitions by detonation on site. This includes both single round detonation in-place and multiple round detonation (or consolidated shots) at a pre-determined location. The procedures for multiple round detonation are described in this paper.

There are two situations that may describe the consolidated shot process: 1) munitions may be collected from anywhere on site and detonated at a designated, sited disposal area or 2) munitions may be collected within a grid and detonated at a designated spot within the grid. In either situation the same procedures, as described in the following paragraphs, must be followed.

2.0 Placement of Munitions

Munitions shall be placed with their sides touching such that their axis is horizontal as shown in Figure 1. The munitions shall be placed so that the nose of each munition is pointing in the same direction. Munitions shall be oriented so that lugs and/or strong-backs, and nose and/or tail plate sections are facing away from personnel locations.

Figure 1 – Placement of Munitions for Consolidated Shots

3.0 Minimum Safe Separation Distance for Intentional Detonations

3.0.1 This document covers procedures for intentional detonations only.

3.0.2 In accordance with DoD 6055.9-STD Chapter 5 paragraph E.4.a(2), the minimum safe separation distance for all personnel will be the greater of the overpressure distance or the appropriate fragment range as determined by the maximum fragment range or the mitigated fragment range.

3.1 Overpressure Distance

In accordance with DoD 6055.9-STD Chapter 5 paragraph E.4.a(2), the allowable overpressure distance will be determined as the scaled distance, K328, based on the total net explosive weight (NEW) of all munitions plus the initiating explosives.

3.2 Fragment Criteria

3.2.1 Maximum Fragment Range

The maximum fragmentation characteristics shall be computed in accordance with HNC-ED-CS-S-98-1. The maximum fragment range shall be computed using these fragmentation characteristics with a trajectory analysis such as the computer software TRAJ. The maximum fragment range shall be the maximum fragmentation distance computed for the most probable munition (MPM) for an OE area at a site, and this shall be the maximum fragment range for a consolidated shot.

3.2.2 Fragment Mitigation

Fragment mitigation may be provided by an appropriate Department of Defense Explosives Safety Board (DDESB) approved engineering control. Typical engineering controls for intentional detonation include tamping and sandbags. The design of such an engineering control shall be based on the maximum fragmentation characteristics of the MPM. The NEW used for the design of the engineering control shall be the total NEW of all munitions plus the initiating explosives. Engineering controls not already approved by DDESB may be submitted (along with appropriate technical data) as part of a site specific explosive safety submission for use at that site. Engineering controls will not be put into use until approved by DDESB and specific applications verified by the appropriate agency; for example, the OE-CX verifies applications for U.S. Army Corps of Engineers.

4.0 Initiation

The consolidated shot shall be initiated in such a manner that detonation of all munitions is simultaneous.

5.0 References

DoD 6055.9-STD, “Department of Defense Ammunition and Explosives Safety Standards”, August 1997.

HNC-ED-CS-S-98-1, Methods for Predicting Primary Fragmentation Characteristics of Cased Explosives, January 1998.

Memorandum, DDESB, DDESB-KO, 27 January 1998, subject: Guidance for Clearance Plans.

ATTACHMENT 3

MITIGATION OF BLAST AND FRAGMENTATION USING SANDBAGS

US Army Corps
of Engineers
Engineering and Support
Center, Huntsville

Use of Sandbags for Mitigation of Fragmentation and Blast Effects Due to Intentional Detonation of Munitions

HNC-ED-CS-S-98-7
AUGUST 1998

DEPARTMENT OF DEFENSE EXPLOSIVES SAFETY BOARD
2461 EISENHOWER AVENUE
ALEXANDRIA, VIRGINIA 22331-0600

DDESB-KO

23 February 1999

MEMORANDUM FOR DIRECTOR US ARMY TECHNICAL CENTER FOR EXPLOSIVES SAFETY (ATTENTION: SIOAC-ES)

SUBJECT: Use of Sandbags for Mitigation of Fragmentation and Blast Effects Due to Intentional Detonations of Munitions, Report HNC-ED-CS-S-98-7 (August 1998)

References: (a) SIOAC-ESL memorandum, dated 30 Nov 98, same subject

(b) Joseph M. Serena and Michelle Crull, "Use of Sandbags for Mitigation of Fragmentation and Blast Effects Due to Intentional Detonations of Munitions, Report HNC-ED-CS-S-98-7," (August 1998)

The subject site plan forwarded by reference (a) has been reviewed with respect to explosives safety criteria. The site plan addresses the use of sandbags, IAW reference (b) to mitigate hazards and protect personnel from intentional detonations of munitions up to the 155-mm M107. Based on the information furnished, the proposed use of sandbags for intentional detonations at ordnance and explosives (OE) sites, IAW reference (b) is approved.

A copy of this site plan package and this letter of approval must be available at OE sites where intentional detonations are conducted that use procedures of this siting package.

Point of contact is Dr. Chester E. Canada, DDESB-KT2 (PH: commercial: 703-325-1369, FAX: 703-325-6227, E-MAIL: canadce@hqda.army.mil).

Daniel T. Tompkins

DANIEL T. TOMPKINS
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cc:
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Use of Sandbags for Mitigation of Fragmentation and Blast Effects Due to Intentional Detonation of Munitions

Prepared by
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August 1998

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Chief, Civil-Structures Division

EXECUTIVE SUMMARY

The U.S. Army Engineering and Support Center, Huntsville (USAESCH) is currently engaged in projects which require the disposal of uncovered/discarded ordnance and explosives (OE) on public and private lands. The uncovered OE item is often detonated in place if it is too dangerous to move. In some cases, covering and tamping with loose earth is used to contain the blast and fragments. Another method to mitigate the fragmentation and blast effects is to cover the item with sandbags. However, traditionally there has been no method to determine the optimum configuration or the required thickness of such a sandbag enclosure.

The Structural Branch, USAESCH, sponsored a test program in 1997 to evaluate the use of sandbag enclosures for fragment and blast mitigation, for intentional detonations at Ordnance and Explosives (OE) sites. Southwest Research Institute (SwRI), under contract to USAESCH, performed a two phase test program of sandbag enclosures. In phase one, the preliminary explosive test phase, four tests on a 155-mm projectile were performed to refine and optimize the test procedure. This test procedure was used in phase two, the comprehensive explosive test phase. In phase two, a total of fourteen tests with five different munitions were performed to determine the thickness of sandbags required to capture all primary fragments. Measurements were made of the overpressures at various places, sandbag throw distances, depth of fragment penetration, and noise levels. High-speed film cameras, video recorders and digital cameras were used to visually record the events.

Required Wall and Roof Thicknesses for Sandbag Enclosures, with Expected Sandbag Throw Distances and Pressures, for Five Tested Munitions

Munition	Charge Weight, Comp B, lb	Required Wall and Roof Sandbag Thickness, in	Expected Maximum Sandbag Throw Distance, ft	Expected Peak Pressure @ 40 feet, psi	Expected Peak Pressure @ 80 feet, psi	Expected Sound Level @ 100 feet, dB
155-mm M107	15.4	36	220	0.18	0.09	115
4.2-in M329A2	8.17 (TNT)	24	125	0.16	0.06	116
105-mm M1	5.08	24	135	0.18	0.08	120
81-mm M374A2	2.1	20	125	0.14	0.05	119
60-mm M49A3	0.43	12	25	0.08	0.03	118

The results of these tests have been used to develop guidelines for the use of sandbag enclosures. The guidelines include required sandbag thicknesses, configuration and construction of the sandbag enclosures, and withdrawal distances based on the greater of sandbag throw distances or 200 ft. This document provides a summary of the test results and these guidelines.

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1.0 Introduction

The U.S. Army Engineering and Support Center, Huntsville (USAESCH) is currently engaged in projects which require the disposal of uncovered/discarded ordnance and explosives (OE) on public and private lands. The uncovered OE item is often detonated in place if it is too dangerous to move. In some cases, covering and tamping with loose earth is used to contain the blast and fragments. Another method to mitigate the fragmentation and blast effects is to cover the item with sandbags. However, traditionally there has been no method to determine the optimum configuration or the required thickness of such a sandbag enclosure.

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The results of these tests have been used to develop guidelines for the use of sandbag enclosures. The guidelines include required sandbag thicknesses, configuration and construction of the sandbag enclosures, and withdrawal distances based on the greater of sandbag throw distances or 200 ft. This document provides a summary of the test results and these guidelines.

2.0 Test Program

2.1 Fragmentation Characteristics of Munitions

Prior to beginning this test program the fragmentation characteristics of a variety of munitions frequently encountered during OE site operations were determined. The fragmentation characteristics were calculated in accordance with procedures outlined in TM5-1300, “Structures to Resist the Effects of Accidental Explosions” [1] and detailed in CEHNC-ED-CS-S-98-1, “Methods for Predicting Primary Fragmentation Characteristics of Cased Explosives” [2]. The fragmentation characteristics were used to predict preliminary thicknesses of sand required to prevent perforation for the five munitions tested.

Optimally, the fragments from the munition will strike the sandbags before the blast wave so that the fragments are penetrating undisturbed sand. To ensure that this will occur it is necessary to reduce the coupling between the explosive charge and the

surrounding soil. This coupling is dependent on the separation distance between the charge and the soil. Full coupling implies that the maximum amount of energy, or velocity, is transferred from the explosive into the soil immediately adjacent to the charge. If an explosive charge is placed in a cavity, so that an air gap exists between the charge and the walls of the cavity, coupling between the explosive and soil is reduced. Therefore, a standoff of some distance is required to reduce the coupling effect. Calculations to determine the velocity of sand particles from a buried explosion were performed. The velocity of the sand particles was compared to the velocity of the design fragment through sand. These calculations suggest that at a distance between 6 and 12 inches from the explosion, the fragment velocity exceeds the particle velocity. Therefore, the initial standoff distances for the tests were 6 and 12 inches.

2.2 Preliminary Explosive Test Phase

In the preliminary explosive tests, four tests of statically detonated 155-mm M107 projectiles were performed. These tests provided the data needed to specify the amount and configuration of sandbags that are required to safely detonate a 155-mm projectile in place, verified that the general test procedure was satisfactory, and defined the instrumentation and data acquisition systems for the subsequent comprehensive explosive tests. Figure 1 shows the site layout for the tests of sandbag enclosures. Although, munitions are rarely oriented vertically for demolition in place, the vertical orientation provided the opportunity to evaluate a greater number of combinations of wall thicknesses and standoff distances. Figures 2 and 3 show the sandbag enclosure configurations for vertical and horizontal weapon tests.

The test matrix for the preliminary explosive tests is shown in Table 1. Two tests were run with the 155-mm in the vertical orientation and two in the horizontal orientation. Each test allowed five standoff distances and five sandbag thicknesses to be evaluated.

The sandbags were made of woven polypropylene, as is commonly used by explosives and ordnance disposal (EOD) personnel, and the volume/weight of the sandbags was either 0.5 ft^3/50 lbs for the large bags or 0.25 ft^3/25 lbs for the small bags. The small bags were used for test two. No additional information was provided by using the small bags so these were not used for any other tests. The bags were filled with a “washed river” sand that was judged to be “typical” by a local soil consultant (Fugro-McClelland Southwest, Inc.).

To determine the sandbag throw distribution some of the sandbags in the first two tests were filled with sand colored with dye. The dye did not improve the quality of the test results. Spray paint was used in the subsequent tests to mark each bag with its original position in the sandbag enclosure. A different color was used to indicate the wall or the roof and numbers were used to indicate the layer in which the sandbag was located.

Detailed descriptions of all tests and results are provided in “Evaluation of Sandbags for Fragment and Blast Mitigation” by Southwest Research Institute [3].

Table 1 – Test Matrix for Preliminary Explosive Tests

Test No.	Orientation	Standoff, in.					Wall Thickness, in. (Bag Size)				Wall Height, in. (Bag Size)	
		S_1	S_2	S_3	S_4	S_R	T_1	T_2	T_3	T_4	H_1	H_2
155-1	Vertical	12	6	6	12	6	32	32.5	45	43	32	20
155-2	Vertical	6	6	6	6	6	18(s)	54	18(s)	53(s)	32	22
155-3	Horizontal	6	6	6	6	6	30	48	24	24	12	30
155-4	Horizontal	6	6	6	6	6	35	36	34	36	12	36

Note: All walls were constructed with large bags, except for those designated with an “s” for small bags.

2.2.1 Preliminary Explosive Test Results

For tests 1 and 2, the 155-mm M107 projectile was detonated using a donor charge of 200 g of C-4 placed in the fuze well and initiated with an Exploding Bridge Wire. For tests 3 and 4, the 155-mm M107 projectile was detonated using a well perforator shaped charge. This approach is typically used for on-site detonations. Time of arrival (TOA) pins were used for all tests to determine if a high order detonation was achieved.

All detonations were high order and results were obtained. The make screens and their frames and the assorted witness screens were scattered across the site. Where possible, each screen was identified and photographed and the number of fragment holes or the condition of the screen was recorded. The results of the first three tests suggested that a wall and roof thickness of 36 inches should be sufficient to contain all of the fragments and to reduce the overpressure levels. The dimensions of test 4 confirmed this configuration.

From the limited data collected on standoff distance, it appears that for standoffs of 6 and 12 inches there is no difference in the thickness of sandbags required to stop fragments. Test 2 showed that the size of the sandbag did not affect the fragment penetration. Test 3 showed that the horizontal orientation of the munition did not greatly effect the fragment penetration. Tests 3 and 4 showed that the base plate of the munition broke up and was stopped by 24 inches or less of sandbags.

The data collected showed that approximately 20 inches of sandbags will completely contain the fragments from the 155-mm M107 projectile. The only indications of fragments exiting the sandbag enclosure came from the two identical 18 inch walls of test 2 (external witness screens on sides 1 and 3 both registered fragment impacts). Internal witness screens at depths of 20 inches to 24 inches for all 4 tests did not indicate any fragment impacts. In tests 2 through 4, the roof witness screens also showed no penetrations for 20 to 36 inches of roof depth. The CONWEP software [4] predicts that 24 inches of sand will stop the design fragment from the 155-mm M107 projectile.

Sandbag throw distances were recorded in 10 foot increments from ground zero to the furthest sandbags. The maximum sandbag throw distances were 150 feet, 191 feet,

157 feet, and 150 feet for tests 1 through 4, respectively. All of the furthest thrown sandbags came from the roof. In most cases, the roof sandbags were found relatively intact while the wall sandbags were often disintegrated. The bulk of the sandbags fell within 100 feet with only a few beyond this distance. An examination of the sandbag throw distances show that the standoff, the size of the bag, and the weapon orientation did not affect the throw distance to any significant degree.

Blast overpressures were recorded for all 4 tests (see Table 2). As shown, the sandbag enclosures greatly reduced the magnitude of the pressure. In test 3, a digital sound meter was placed 100 feet from ground zero and the maximum sound level recorded was 114.7 decibels.

Table 2 – Blast Overpressures from Preliminary Explosive Tests

Test No.	Side 1				Side 4			
	P1 @ 40', psi	P2 @ 40', psi	P3 @ 80', psi	P4 @ 80', psi	P5 @ 40', psi	P6 @ 40', psi	P7 @ 80', psi	P8 @ 80', psi
155-1	0.67	0.71	ND	ND	0.37	0.38	ND	ND
155-2	1.31	1.18	ND	ND	0.74	0.97	ND	ND
155-3	0.16	0.16	0.07	0.06	0.16	0.18	0.09	ND
155-4	0.04	0.04	0.03	0.03	0.07	0.08	ND	0.05

ND = no data

2.3 Comprehensive Explosive Tests

An additional fourteen tests were performed: one more using 155-mm M107 projectiles, four using 105-mm M1 projectiles, three using 4.2-in M329A2 projectiles, four using 81-mm M374A2 mortars, and two using 60-mm M49A3 mortars. The test matrix for the comprehensive explosive tests is shown in Table 3. For all tests performed with the munition in the vertical orientation, detonation was achieved using a donor charge of 100 grams (50 grams for test 60-1) of C-4 in the fuze well. For all tests performed with the munition in the horizontal orientation, detonation was achieved using a well perforator. TOA pins were used for all tests to check if a high order detonation was achieved.

For each of the comprehensive explosive tests, woven polypropylene 0.5 ft^3 sandbags were filled with 50 lbs of washed river sand. The sandbags were painted and numbered as described in Section 2.2 to indicate their original position in the sandbag enclosure. Moisture content was not controlled nor monitored during the test program.

Pressure gages, a sound meter, high speed cameras, digital cameras and video cameras were used for data acquisition during each test. Internal and external witness screens were used to determine how deeply the fragments moved into the sandbag mass and whether any fragments exited the sandbag enclosure.

Table 3 – Test Matrix for Comprehensive Explosive Tests

Test No.	Orientation	Standoff, in.					Wall Thickness, in.				Wall Height, in.	
		S_1	S_2	S_3	S_4	S_R	T_1	T_2	T_3	T_4	H_1	H_2
155-5	Horizontal	7	7	5	6	7	36	36	36	36	13	36
4.2-1	Vertical	5.5	5.5	5.5	5.5	6	20	24	31	36	19	24
4.2-2	Horizontal	6.5	6.5	6	6	7	24	25	24	24	11	24
4.2-3	Horizontal	6	5	5	6	7	24	25	25	24	11	24
105-1	Vertical	5.5	5.5	5.5	5.5	6	20	26	31	35	25	24
105-2	Vertical	0	0	4	6	6	29	25	19	25	26	23
105-3	Horizontal	7	5	5	5	9	24	24	24	24	13	24
105-4	Horizontal	6.5	6	5	6	7	25	25	24	24	11	23
81-1	Vertical	5	5	6	6	6	12	19	23	30	15	18
81-2	Horizontal	7	6	5.5	7	6	18	24	18	24	9	18
81-3	Horizontal	7	6	5	6	7	18	19	18	19	10	18
81-4	Horizontal	6	5.5	5.5	5.5	8	19	20	19	20	11	18
60-1	Vertical	6	6	6	6	6	13	19	23	30	11	12
60-2	Horizontal	6.5	3	5.5	3	6	12	12	12	12	8	13

All detonations were high order and results were obtained. The assorted witness screens were scattered across the site. Where possible, each screen was identified and photographed and the number of fragment holes or the condition of the screen was recorded. Sandbag throw distances were recorded in 10 foot increments from ground zero to the furthest sandbags. Blast overpressures were recorded for all tests at 40 feet and 80 feet from ground zero. A digital sound meter was placed 100 feet from ground zero. A summary of the results is shown in Table 4.

The final test for each munition was a confirmation test. These included tests 155-5, 4.2-3, 105-4, 81-3 and 60-2. The purpose of the confirmation tests was to model as closely as possible the actual use of sandbags in field conditions. In each test the internal witness screens were omitted. Sandbags were staggered both horizontally and vertically. External witness screens were placed over the roof and the two sides facing away from the pressure gages. After each test, the external witness screens were recovered and inspected for fragment penetrations. No such penetrations were identified. Therefore, the sandbag thicknesses defined in Table 4 are those used in the confirmation tests. For two munitions, the penetration data from internal witness panels suggests that somewhat smaller sandbag thicknesses may be sufficient to capture all fragments. As stated above for the 155-mm M107, internal witness screens show no fragment penetrations for sandbag thicknesses of about 24 inches or more. For the 4.2-inch M329A2 mortar, the internal witness screens show no fragment penetrations deeper than about 18 inches. However, the thicknesses of 36 inches for the 155-mm M107 and 24 inches for the 4.2-inch M329A2 are retained for use in the field, since sandbag throw distances are based on these thicknesses. While possibly thicker than necessary from capturing fragments, the increased total mass of the sandbags results in reduced sandbag throw distances.

Detailed descriptions of all tests and results are provided in “Evaluation of Sandbags for Fragment and Blast Mitigation” by Southwest Research Institute [3].

3.0 Guidelines for Use of Sandbags

3.1 Enclosure Geometry

Table 5 summarizes the results of the tests. This table specifies the minimum thickness of sandbag walls and roof that is needed to completely contain the fragments for the five munitions that were tested in this project. It also gives the expected maximum sandbag throw distances, the peak pressures at 40 feet and 80 feet, and the sound level at 100 feet, for the five munitions. For safety and conservatism, the expected sandbag throw distances are approximately 10% larger than the largest distances actually measured in the tests. Thus, the expected sandbag throw distances given in Table 5 are conservative in two ways: first, the largest measured sandbag throw distance from all tests of a particular round is used and second, this value is increased by 10%. Due to the already low values of peak pressures, a similar increase in the expected peak pressures was not deemed necessary or justified.

Table 4 – Summary of Results from Comprehensive Explosive Tests

Munition	Sandbag Thickness (in) to Defeat Fragments	Max. Sandbag Throw Distance (ft)		Max Peak Overpressure (psi) @ 40 ft		Max Peak Overpressure (psi) @ 80 ft		Max Noise Level (dB) at 100 ft
		Side of Round	Nose/Tail of Round	Side of Round	Nose of Round	Side of Round	Nose of Round	
155-mm M107	36	200	130	0.06	0.12	0.04	0.05	114.7
4.2-in M329A2	24	110	70	0.12	0.14	0.04	0.06	115.8
105-mm M1	24	120	50	0.17	0.18	0.07	0.08	119.3
81-mm M374A1	20	110	30	0.14	0.08	0.05	0.03	118.3
60-mm M49A3	12	20	20	0.06	0.08	0.02	0.03	117.3

Obviously, the five munition types do not cover all of the munitions that may be encountered. To determine the minimum wall and roof thickness for a particular shell other than those found in Table 5, the approach is as follows:

(1) Determine the initial fragment velocity (V_F) in ft/s, the maximum fragment weight (W_F) in pounds, and the kinetic energy ($W_F V_F^2/2$) in lb-ft^2/s^2 for the particular munition.

(2) Identify the munition with the next largest kinetic energy, from Table 6.

(3) Use the sandbag wall and roof thickness from Table 5 for the munition with the next largest kinetic energy shown in Table 6.

Table 6 provides the maximum fragment weight, the initial fragment velocity, and the resulting kinetic energy for the 5 munition types. The maximum fragment weight and the initial fragment velocity values were determined with the Mott and Gurney equations, as presented in TM 5-1300 [1] and detailed in HNC-ED-CS-S-98-1 [2].

Table 5 - Required Wall and Roof Thicknesses for Sandbag Enclosures, with Expected Sandbag Throw Distances and Pressures, for Five Tested Munitions

Munition	Charge Weight, Comp B, lb	Required Wall and Roof Sandbag Thickness, in	Expected Maximum Sandbag Throw Distance, ft	Expected Peak Pressure @ 40 feet, psi	Expected Peak Pressure @ 80 feet, psi	Expected Sound Level @ 100 feet, dB
155-mm M107	15.4	36	220	0.18	0.09	115
4.2-in M329A2	8.17 (TNT)	24	125	0.16	0.06	116
105-mm M1	5.08	24	135	0.18	0.08	120
81-mm M374A2	2.1	20	125	0.14	0.05	119
60-mm M49A3	0.43	12	25	0.05	0.03	118

Table 6 - Maximum Fragment Weight, Initial Fragment Velocity and Kinetic Energy for Five Tested Munitions

Munition	W_F, Maximum Fragment Weight, lb	V_F, Initial Fragment Velocity, ft/s	Kinetic Energy, 10^6 lb-ft^2/s^2
155-mm M107	0.467	4667	5.085
4.2-in M329A2	0.079	6391	1.613
105-mm M1	0.155	4870	1.868
81-mm M374A2	0.031	6721	0.700
60-mm M49A3	0.033	3605	0.214

As an example, for a shell such as the 3-in Stokes Mortar Round, the maximum fragment weight and initial fragment velocity are 0.0436 lb and 6189 ft/s, respectively. The resulting kinetic energy is 0.835 x 10^6 lb-ft^2/s^2. The next largest fragment kinetic energy in Table 6 is the 4.2-in M329A2 round. Therefore, a sandbag enclosure with a roof and wall thicknesses of 24 inches should be used to contain the fragments and suppress the blast overpressures. The maximum sandbag throw distance is 125 ft. Therefore, the withdrawal distance is 200 ft.

Based on this procedure, a more complete list of typical munitions is given in Table 7. This table includes the required sandbag wall and roof thicknesses and maximum expected sandbag throw distances to be used for each munition. For other munitions not listed in Table 7, the procedure given above can be used. The procedure should not be used to extrapolate sandbag thicknesses or sandbag throw distances for munitions larger than the 155-mm M107.

3.2 Enclosure Construction Method

The enclosure construction method follows the procedure that was used to build the test enclosures, with a few modifications. Figure 4 illustrates a typical enclosure. Figure 5 shows a photograph of a sandbag enclosure for an 81 mm mortar.

The sandbag fabric should be woven polypropylene. Each bag should have a nominal volume of 0.5 ft^3 and an approximate weight when full of 50 lb. The bags should be filled with washed sand, either dry or in saturated surface dry (that is, slightly moist) condition. Wet sand should not be used. Prefilled sandbags should be protected from the rain by storage on pallets, off the ground surface, and by covering them with a plastic tarpaulin or similar cover to prevent them from becoming saturated with water. The gradations and physical composition of the sand are not critical but it should be at least typical of local construction practice for sand used in foundations and backfill. Minor inclusions of clay or soils materials can be permitted. However, no rocks or stones should be placed in the sandbags. Typically, the sand used for the tests had a density of about 100 pounds per cubic foot and a moisture content of 6-7%.

Four walls of identical thickness should surround the munition. The minimum wall thickness should be the thickness determined using the procedure in Section 3.1 above. The sandbag walls should be stacked to maintain a clear standoff distance of 6 inches between the shell and the inside face of each wall. The interior face of each wall should be vertical but the exterior face can be built with a 1:6 slope (2" horizontal to 12" vertical). If a sloped outer face is used, the thickness of the wall, at the nominal “top” of the wall, 6 inches above the top of the munition, must be no less than the specified required thickness

The sandbags should be placed tightly against each other. All vertical joints should be staggered, so there is no clear line of sight from the munition to the exterior. As the wall is built, each new layer of sandbags should run in opposite direction to the layer below, so that the layers are interlocked (see Figure 6).

At a minimum, a double layer of sandbags shall be used. For example, when a 12” thickness is required, the sandbags should be oriented so that two sandbags are necessary to achieve this thickness (see Figure 7).

After the walls are constructed to a height of 6" above the upper surface of the munition, the shaped charge or other initiator should be placed on the shell. Ideally, the use of shaped charges, such as oil well perforators, is recommended. These add very little to the total charge weight for each detonation, given the highly directional nature of the effects of the shaped charge. Also, the use of shaped charges for initiation parallels test procedures. The shaped charge should be located either on top of the munition or on its side. If it is located on the side of the round, the charge should be tilted downward sufficiently to ensure that the shaped charge jet penetrates the round and is directed into the ground, rather than into the opposite sandbag wall. Generally, a small mound of sand next to the round can be used to establish this orientation.

A sheet of 3/4-inch thick Douglas Fir (or equivalent) plywood should be cut to the dimensions of the cavity between the walls, plus 12 inches in each direction. The plywood sheet is then centered on the walls so that it bears on 6" of each wall. The additional sandbags that make up the roof of the enclosure are then placed on top. As with the side walls, the roof sandbags should be stacked with staggered horizontal joints and alternating directions in each layer. The exterior sides of the roof may also be vertical or have a 1:6 slope. The thickness of the sandbag roof, above the plywood panel, must be the same as the required wall thickness.

After the sandbag layers of the roof have been placed to the correct height, the enclosure is complete and the munition may be detonated.

Table 7 - Required Wall and Roof Thicknesses for Sandbag Enclosures, with Expected Sandbag Throw Distances and Pressures, for Tested and Non-Tested Munitions

Munition	Charge Weight (lb)	W_F, Maximum Fragment Weight, lb	V_F, Initial Fragment Velocity, ft/s	Kinetic Energy, 10^6 lb-ft^2/s^2	Required Wall and Roof Sandbag Thickness, in	Expected Maximum Sandbag Throw Distance, ft	With-drawal Distance, ft
155mm M107*	15.48	0.467	4667	5.086	36	220	220
4.7-in Mark I	6.07	0.591	3566	3.761	36	220	220
105mm M1*	5.08	0.155	4870	1.840	24	135	200
4.2-in M329A2*	8.165	0.079	6391	1.607	24	125	200
4-in Stokes	7.92	0.078	6336	1.570	24	125	200
75mm M48	1.47	0.153	3471	0.922	24	125	200
3-in Stokes	2.1	0.044	6189	0.835	24	125	200
2.75-in M229 Rocket	4.8	0.050	5569	0.777	24	125	200
81mm M374*	2.1	0.031	6721	0.696	20	125	200
37mm MK II	0.53	0.030	5758	0.490	20	125	200
60mm M49A3*	0.42	0.024	5114	0.310	12	25	200
FMU 54A/B	0.357	0.006	9031	0.263	12	25	200
40mm MK2 Mod 0	0.187	0.033	3605	0.215	12	25	200
MK II Grenade	0.125	0.014	3425	0.083	12	25	200
25mm M792	0.096	0.005	5736	0.081	12	25	200
M67 Grenade	0.40625	0.001	7006	0.029	12	25	200
20mm M56A4	0.0264	0.0000011	4941	0.004	12	25	200

* = tested munitions

3.3 Withdrawal Zone

A withdrawal zone is necessary for any detonation. This withdrawal zone applies to everyone, both public and operational personnel. The withdrawal zone is the maximum of the sandbag throw distance, the distance to a sound level of 140 db, or 200 ft. For all munitions tested, the sound level at 100 ft was substantially less than 140 db. At 200 ft. the sound level will be even lower. The withdrawal zones are also listed in Table 7.

4.0 Summary and Conclusions

A test program has been performed to determine the effects of sandbag enclosures for mitigating fragments and blast effects due to an intentional detonation of a munition. A total of eighteen tests on five different munitions were performed. A summary of the test procedures and results are presented in this document.

The results of these tests have been used to develop guidelines for the use of sandbag enclosures to mitigate the fragments and blast effects due to an intentional detonation of a munition. Methods for determining the required sandbag thickness and the resulting sandbag throw distance are detailed in Section 3.0. Figures 4, 5, 6 and 7 show the resulting sandbag enclosures.

5.0 References

1. TM5-1300, “Structures to Resist the Effects of Accidental Explosions”, Departments of the Army, the Navy, and the Air Force, November 1990.

2. HNC-ED-CS-S-98-1, “Methods for Predicting Primary Fragmentation Characteristics of Cased Explosives”, M. Crull, U.S. Army Engineering and Support Center, Huntsville, January 1998.

3. “Evaluation of Sandbags for Fragment and Blast Mitigation”, D. Stevens, Southwest Research Institute, San Antonio, TX, January 1998.

4. “User’s Guide for Microcomputer Programs CONWEP and FUNPRO Applications of TM 5-855-1. “Fundamentals of Protective Design For Conventional Weapons””, Revision 2, D. Hyde, US Army Corps of Engineers Waterways Experiment Station, February 1989.

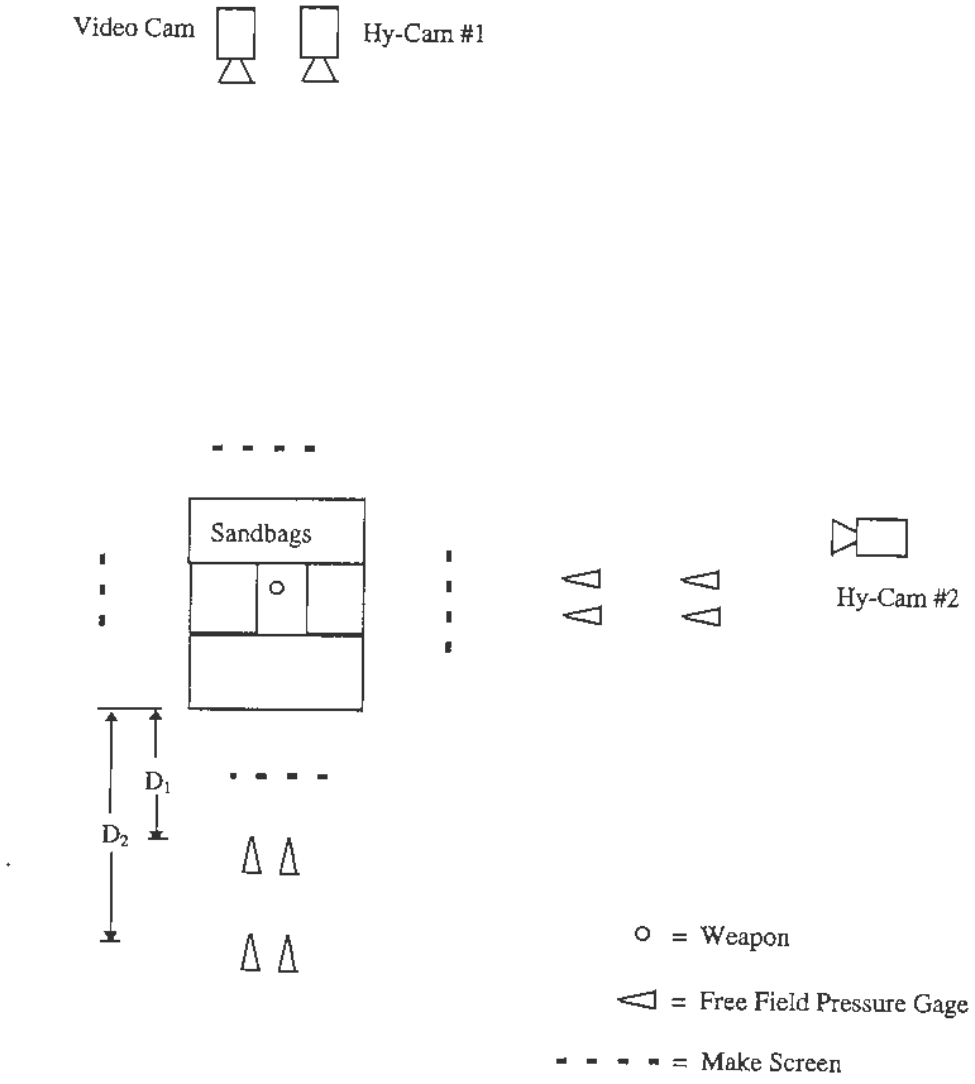


Figure 1 – Site Layout for Tests of Sandbag Enclosures

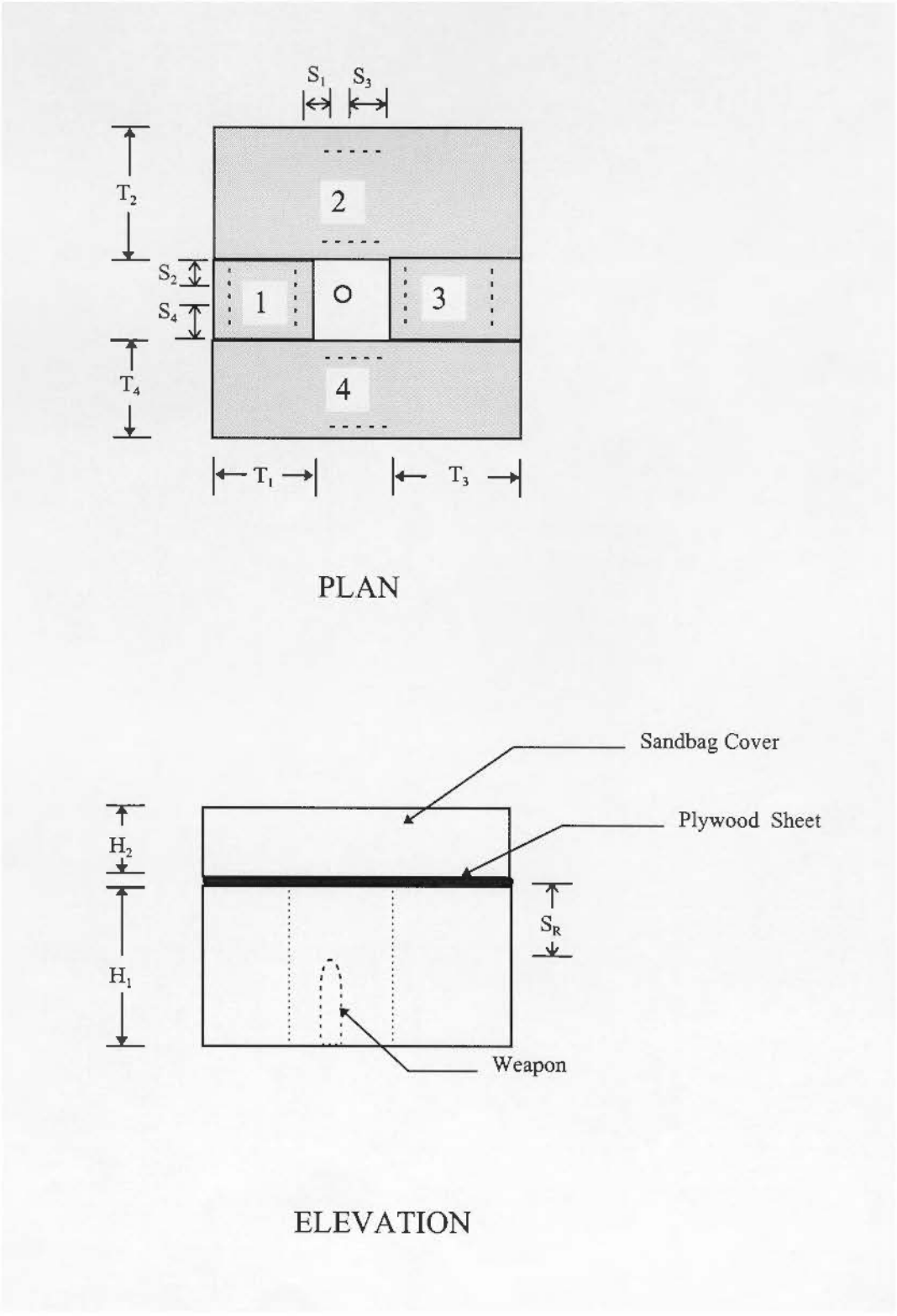


Figure 2 – Sandbag Enclosure Configuration for Vertical Weapon Tests

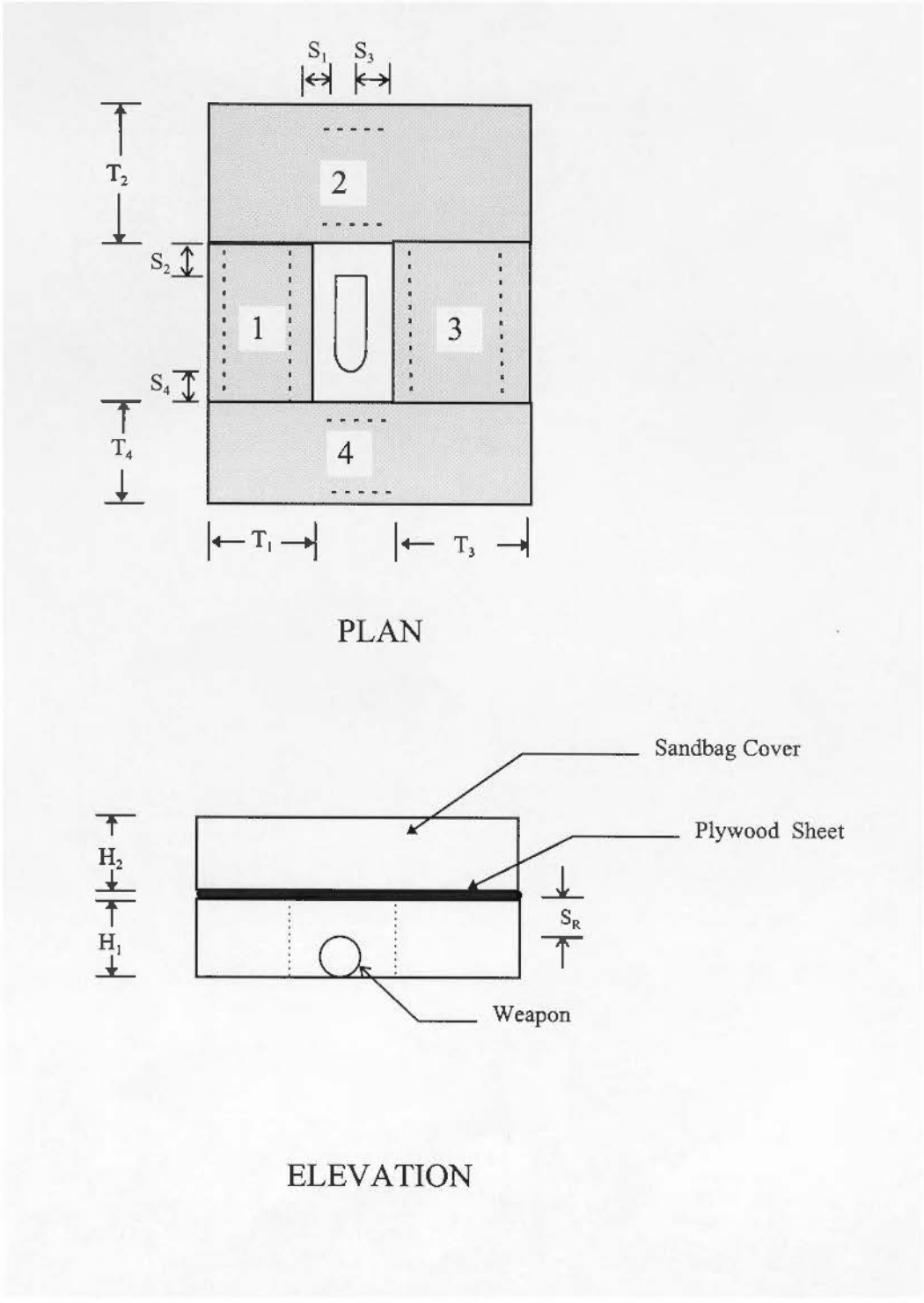


Figure 3 – Sandbag Enclosure Configuration for Horizontal Weapon Tests

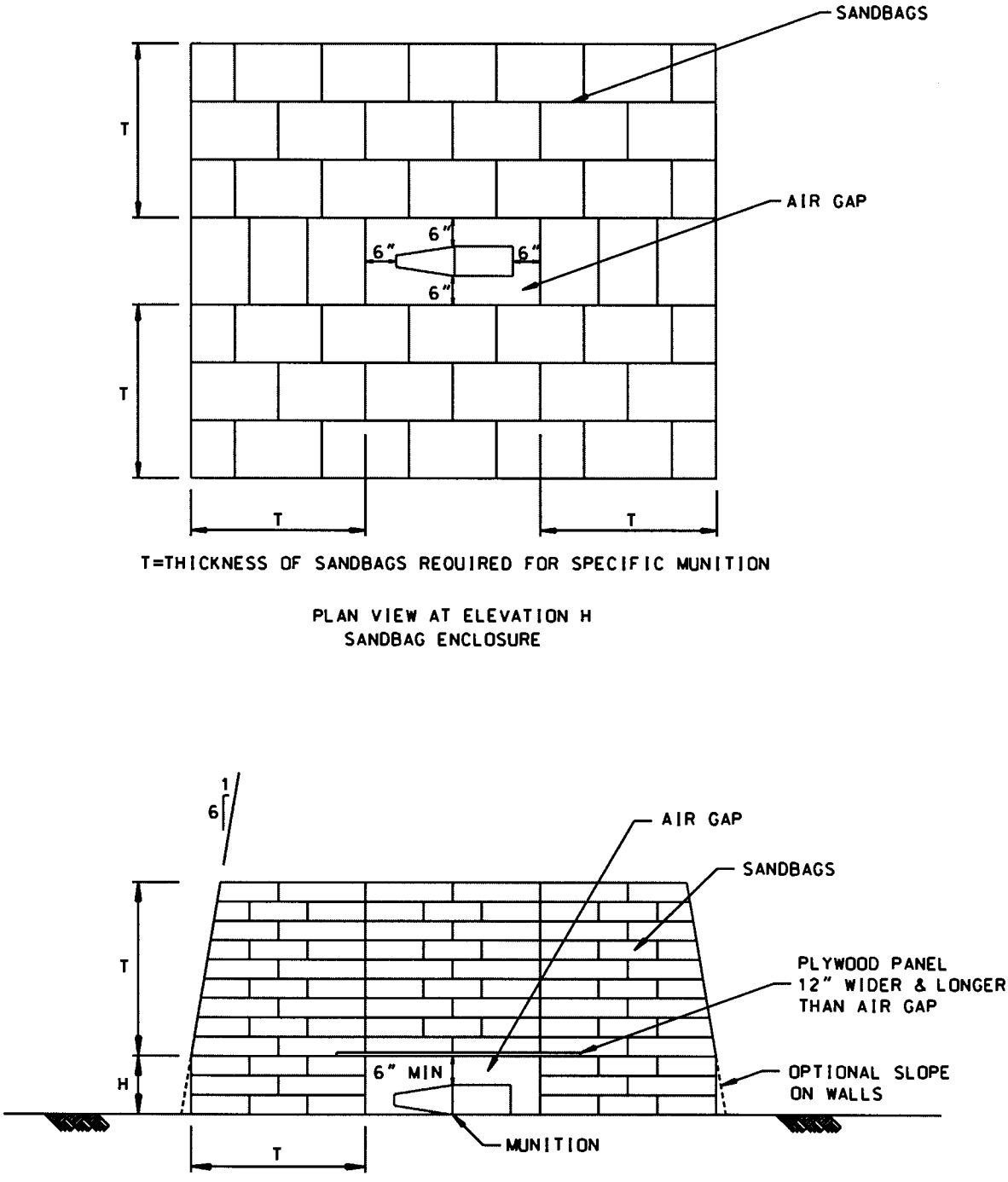
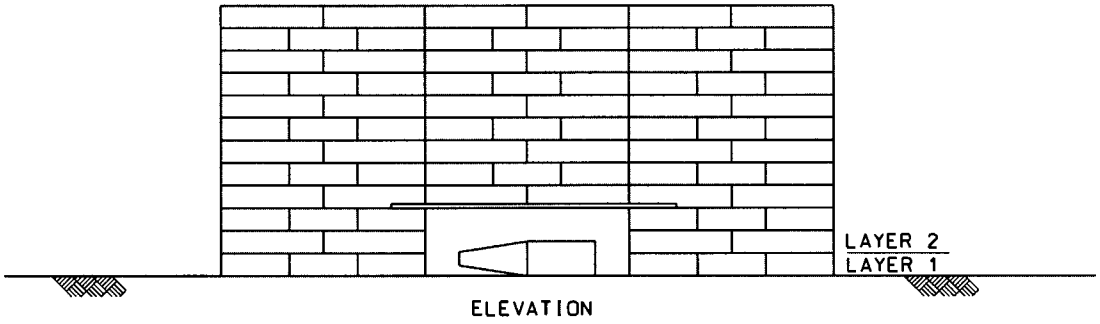
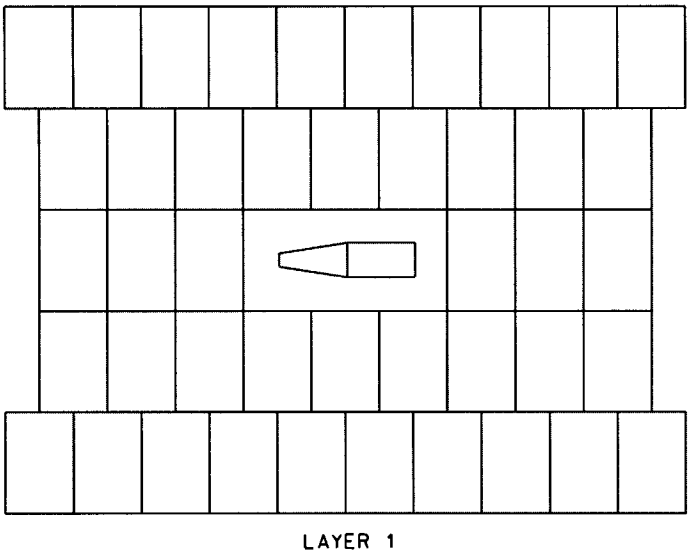


Figure 4 - Typical Sandbag Enclosure

Figure 5 – Sandbag Enclosure for an 81 mm M374A2 mortar.





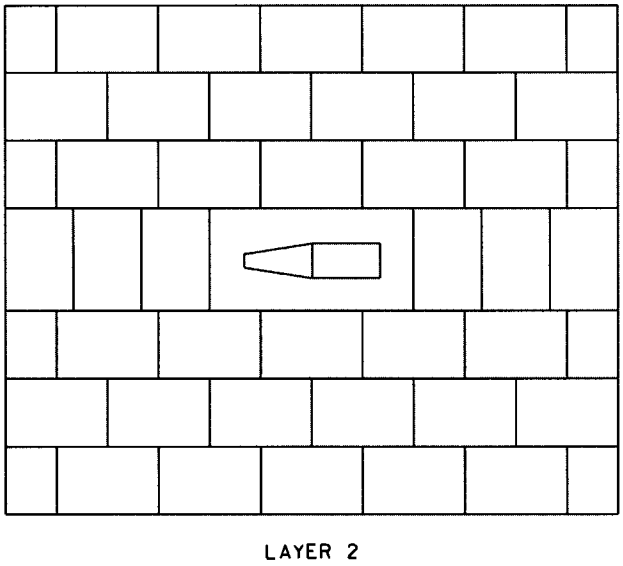


Figure 6 - Interlocking Alternate Layers of Sandbags

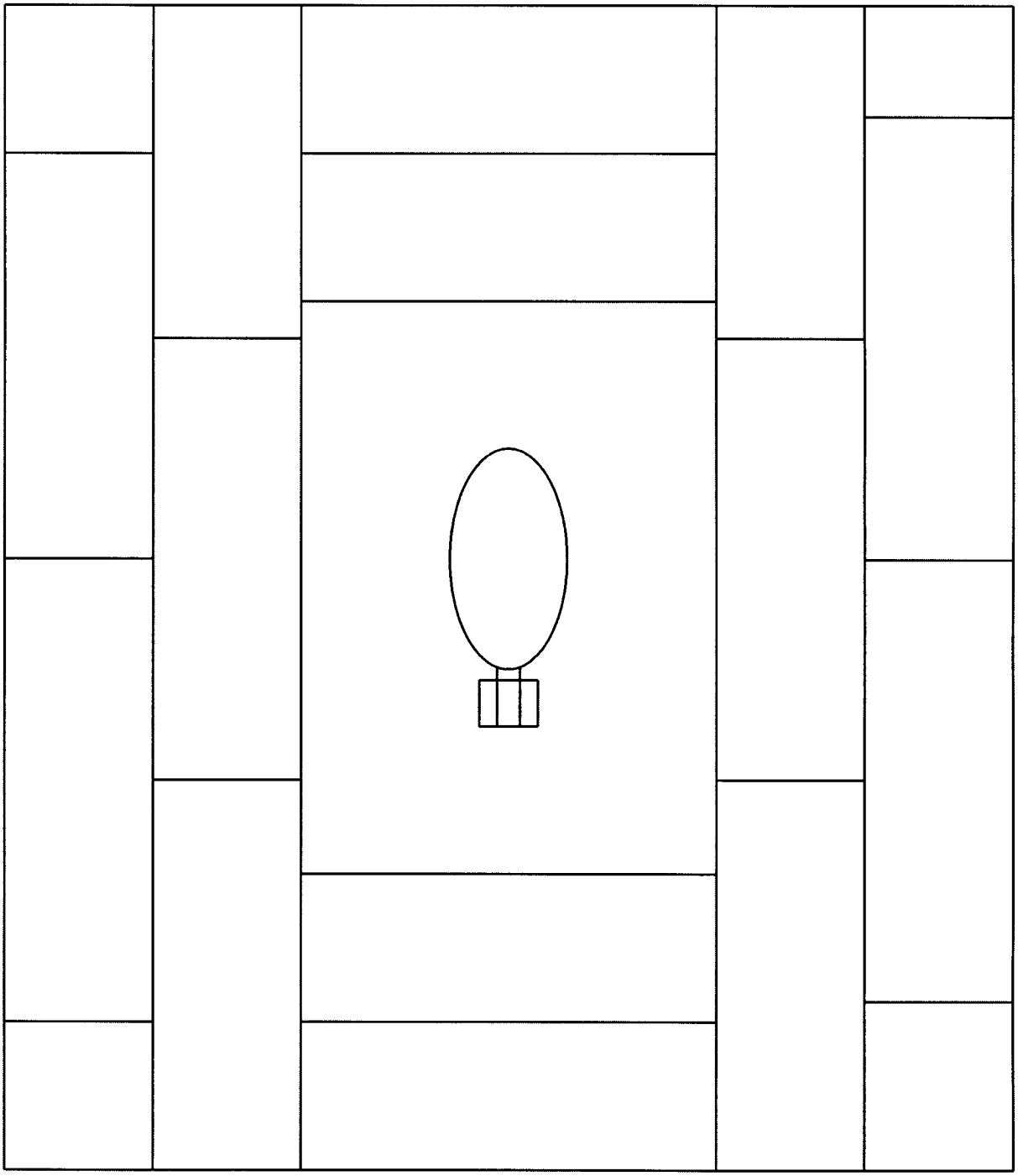


Figure 7 - Configuration for 12” Wall Enclosures

ATTACHMENT 4

MITIGATION OF BLAST AND FRAGMENTATION USING WATER

US Army Corps of Engineers
Engineering and Support Center, Huntsville

USE OF WATER FOR MITIGATION OF FRAGMENTATION AND BLAST EFFECTS DUE TO INTENTIONAL DETONATION OF MUNITIONS

HNC-ED-CS-S-00-3
SEPTEMBER 2000

DEPARTMENT OF DEFENSE EXPLOSIVES SAFETY BOARD
2461 EISENHOWER AVENUE
ALEXANDRIA, VIRGINIA 22331-0600

27 FEB 2001

DDESB-KT

MEMORANDUM FOR US ARMY DEFENSE AMMUNITION CENTER
(ATTENTION: SMAAC-ESL)

SUBJECT: Use of Water for Mitigation of Fragmentation and Blast Effects Due to Intentional Detonations of Munitions, Report HNC-ED-S-00-3 (December 2000)

Reference: SMAAC-ESL (CESO-E/19 Dec 00) (385[A]) 1st End dated 21 December 2000, Subject: Explosives Safety Submission (ESS) for Use of Water for Mitigation of Fragmentation and Blast Effects Due to Intentional Detonations of Munitions, HNC-ED-S-00-3, September 2000

The Department of Defense Explosives Safety Board (DDESB) Secretariat has reviewed the mitigation technology described in the subject report as requested by the reference. Based on the information furnished in the report the water mitigation techniques for intentional detonations defined in Section 3.0 of the report are approved for field use in Ordnance Explosives (OE) removal action projects.

A copy of this memorandum of approval must be included with a DDESB approved site plan, and be available at OE sites where intentional detonations are conducted that use the approved water mitigation technique.

The DDESB point of contact for this action is Dr. Jerry M. Ward, Director, Technical Programs Division, DSN: 221-2525, Commercial phone: (703) 325-2525; Fax: (DSN) 221-6227 and E-mail: Jerry.Ward@hqda.army.mil.

DANIEL T. TOMPKINS
Colonel, USAF
Chairman

USE OF WATER FOR MITIGATION OF FRAGMENTATION AND BLAST EFFECTS DUE TO INTENTIONAL DETONATION OF MUNITIONS

HNC-ED-CS-S-00-2

FEBRUARY 2000

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Chief, Structural Branch

Approved by: _____

PAUL M. LAHOUD DATE
Chief, Civil-Structures Division

EXECUTIVE SUMMARY

The U.S. Army Engineering and Support Center, Huntsville (USAESCH) is currently engaged in projects which require the disposal of uncovered/discarded ordnance and explosives (OE) on public and private lands. The uncovered OE item is often detonated in place if it is too dangerous to move. In some cases, covering and tamping with loose earth is used to contain the blast and fragments. Another method to mitigate the fragmentation and blast effects is to cover the item with sandbags. However, both of these methods result in secondary fragments (earth clumps or sandbags) being thrown some distance from the blast. Preliminary tests show that water can be used to mitigate the fragmentation and blast effects and, depending on the method used to contain the water, there may be no hazardous secondary fragments. In addition, the water quenches the fireball and there is no fire hazard associated with the detonation. This last observation is especially important when working in a high fire hazard area.

The Structural Branch, USAESCH, sponsored a test program in 1999 to evaluate the use of water for fragment and blast mitigation, for intentional detonations at Ordnance and Explosives (OE) sites. The U.S. Army Engineer Research and Development Center (USAERDC), with USAESCH performed a two-phase test program of water mitigation of blast and fragmentation. In phase one, tests were conducted using four different munitions to determine the depth of water required to defeat the fragments. In phase two, different water containment systems were tested for these munitions.

For phase one, the munitions were suspended vertically in an aboveground pool in an off-center position. Thus the fragments were dispersed through varying thicknesses of water. Witness panels of 0.032” aluminum were used to record any fragments that might exit the pool. Witness screens were placed in the pool at various distances from the munition to determine if the fragments had penetrated that far.

Once a required water thickness was determined for each of the four munitions in phase one, containers were selected to test for use in actual disposal situations. The points considered in this selection were adaptability to munition size, transportability (empty or pre-filled with water), debris producing potential, adaptability to uneven terrain, and cost. The water containment systems tested were 55-gallon plastic drums, 1100-gallon plastic agricultural chemical tanks, 5-gallon stackable plastic carboys, and inflatable plastic wading pools.

These tests showed that water is a feasible means of mitigating fragments and blast effects from an intentional detonation. The containers that are made of heavy plastic produce secondary fragments that may be thrown some distance from the blast. The inflatable swimming pools did not produce any significant secondary fragments. Some small pieces of these pools were found around the site but, since the pool was made of thin flexible plastic, these pieces were very

lightweight and not hazardous. High-speed photography of the tests shows that there is no fireball. Therefore, there is no fire hazard associated with the detonation.

The results of these tests have been used to develop guidelines for the use of water to mitigate fragments and blast effects due to an intentional detonation of a munition. Methods for determining the required water containment system and the resulting minimum separation distance are detailed in this report. Figures are provided to show the resulting munition/initiator configuration and water containment systems.

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1.0 INTRODUCTION

The U.S. Army Engineering and Support Center, Huntsville (USAESCH) is currently engaged in projects which require the disposal of uncovered/discarded ordnance and explosives (OE) on public and private lands. The uncovered OE item is often detonated in place if it is too dangerous to move. In some cases, covering and tamping with loose earth is used to contain the blast and fragments. Another method to mitigate the fragmentation and blast effects is to cover the item with sandbags. However, both of these methods result in secondary fragments (earth clumps or sandbags) being thrown some distance from the blast. Preliminary tests show that water can be used to mitigate the fragmentation and blast effects and, depending on the method used to contain the water, there may be no hazardous secondary fragments. In addition, the water quenches the fireball and there is no fire hazard associated with the detonation. This last observation is especially important when working in a high fire hazard area.

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site but, since the pool was made of thin flexible plastic, these pieces were very lightweight and not hazardous. High-speed photography of the tests shows that there is no fireball. Therefore, there is no fire hazard associated with the detonation.

2.0 TEST PROGRAM

The munitions used in both phases of the tests are the 60 mm M49A4 mortar, the 81 mm M362A1 mortar, the 105 mm M1 projectile and the 155 mm M107 projectile.

2.1 Phase One Tests

Commercially available aboveground swimming pools were used to contain the water in the phase one tests because they were easily obtainable and relatively inexpensive. Different size pools were used for different munitions. In the phase one tests the munitions were suspended vertically in the pool at a specified distance from the edge of the munition to one edge of the pool (off-center). Window screens were suspended from 2”x2” wood beams 180 degrees from the nearest edge of the pool at specified distances from the munition. These were used as witness panels in the pool. Witness panels of 0.032” aluminum were placed around the outside of the pool to record any fragments that might leave the pool. The test layout is shown in Figure 1 and the dimensions of the pool and placement of the munition and witness screens are shown in Table 1. The detonations were initiated using C-4 packed in the fuze well.

TABLE 1 – Phase One Test Parameters

Munition	Pool Diameter	Distance, R1 Edge of Pool	Expected Penetration	Pool Depth	Munition Distance from		Munition to Screen Distance			
					Bottom	Surface	S1	S2	S3	S4
60mm	90"	6"	8"	18"	2"		5"	10"	15"	20"
81mm	90"	12"	18"	24"	2"		10"	15"	20"	25"
105mm	12'	24"	30"	24"	3.5"	3"	30"	30"	40"	50"
155mm	18'	36"	48"	46"	4"	15"	40"	50"	60"	70"

2.1.1 155 mm M107 Projectile

The 155 mm M107 projectile contains 15.4 lbs of Comp B. For the phase one test, the booster was removed and the fuze well was packed with C-4. An 18 ft diameter, 4 ft deep pool was used for this test. The projectile was placed base down to make sure the base plate did not become airborn. Fragments were found all around the pool. One section of the metal pool wall from the near blast region was wrapped in a witness panel and thrown over 200 feet from ground zero.

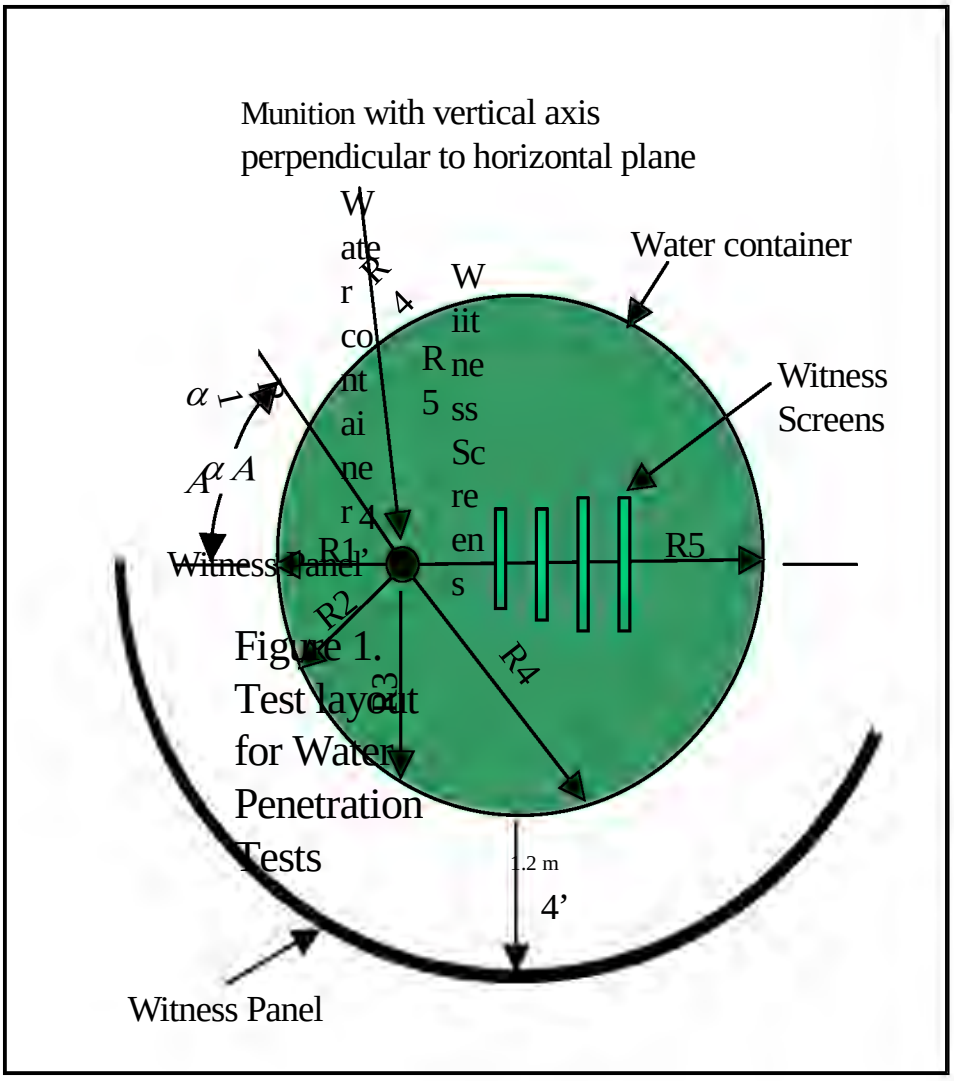


Figure 1. Test layout for Water Penetration Tests

FIGURE 1 – Test Layout for Phase One Tests

TABLE 2 – 155 mm M107 Phase One Results

Perforation of Pool			Fragment Size		Comments	Witness Screens	
Angle A, degrees	Distance D, in.	Height, in.	Length, in.	Width, in		Screen No.	Distance, in.
40.54	70.31		2	1.5		1	24
59.93	96.46		4	2		2	30
66.45	104.96		1	0.125		3	40
						4	50
						5	60
						6	70

Note: Fragment penetrated 5th screen but not 6th.

2.1.2 105 mm M1 Projectile

The 105 mm M1 projectile contains 5.07 lbs of Comp B. For the phase one test the fuze well was packed with C-4. A 12 ft diameter, 2 ft deep pool was used for this test. The projectile was placed base down to make sure the base plate did not become airborn. Fragments were recovered out to a distance of approximately 75 feet from the pool. There were no penetrations in the side or rear of the pool or witness panels, so the explosive mass apparently lofted these fragments along with the water.

TABLE 3 – 105 mm M1 Phase One Results

Perforation of Pool			Fragment Size		Comments	Witness Screens	
Angle A, degrees	Distance D, in.	Height, in.	Length, in.	Width, in		Screen No.	Distance, in.
25.97	38.87	28	5	1		1	30
47.96	53.83	12	6	1	Tear?	2	42
						3	54
						4	66
						5	80

Note: Fragment penetrated 1st screen only.

2.1.3 81 mm M362A Mortar

The 81 mm M362A mortar contains 2.1 lbs of Comp B. For the phase one test the fuze well was packed with 113 grams of C-4. A 90 inch diameter, 24 inch deep pool was used for this test. The mortar was placed nose down in the pool with the nose 2 inches off the bottom. No fragments penetrated the rear side of the pool. The tail fin was recovered 42 feet from the pool. One fragment was recovered 130 feet from the pool.

TABLE 4 – 81 mm M362A Phase One Results

Perforation of Pool			Fragment Size		Comments	Witness Screens	
Angle A, degrees	Distance D, in.	Height, in.	Length, in.	Width, in		Screen No.	Distance, in.
2.56	12.12	17	2.5	0.25		1	10
2.56	12.12	17	1.5	0.125	Dent	2	15
1.79	12.06	36	0.25	2		3	20
7.62	13.05	7	4	2		4	25
7.34	12.97	5	1	0.25	Dent		
7.62	13.05	9	0.75	0.5			
8.46	13.28	12	1	0.5	3 together		
9.61	13.63	14	0.25	0.25	Frag imbedded		
7.62	13.05	22	0.5	0.25			
7.34	12.97	33	2	1			
7.89	13.12	36	1	0.5			
10.50	13.92	9	3	1			
10.80	14.02	37	0.75	0.75			

Note: Fragment penetrated 3rd screen but not 4th.

2.1.4 60 mm M49A4 Mortar

The 60 mm M49A4 mortar contains 0.42 lbs of Comp B. For the phase one test the fuze well was packed with 65.2 grams of C-4. A 90 inch diameter, 18 inch deep pool was used for this test. The mortar was placed nose down in the pool with the nose 2 inches off the bottom. The pool was filled to the top (22 inch depth) but no effort was made to level the ground under the pool. As a result the low side of the pool began to sag before the test. Sandbags were used to prop up this side. No fragments penetrated the rear of the pool, but were found in the bottom of the pool. Fragment holes were found in the lower portion of the witness panel. Several fragments were found 30 to 40 feet from the pool, but the fragment field extended only 30 degrees off a line running through the center of the munition to the nearest point on the side of the pool. No fragments were found in the same region behind the witness panel side, although several fragments penetrated the witness panel.

TABLE 5 – 60 mm M49A4 Phase One Results

Perforation of Pool			Fragment Size		Comments	Witness Screens	
Angle A, degrees	Distance D, in.	Height, in.	Length, in.	Width, in		Screen No.	Distance, in.
2.97	7.32	10	1.75	1.25		1	5
6.07	8.26	4	2.25	0.25		2	10
6.07	8.26	12	0.5	0.125		3	15
6.67	8.49	4	1	0.125	dent	4	20

Note: Fragment penetrated 1st screen but not 2nd.

2.1.5 Phase One Summary and Conclusions

Open front barricade tests using the 60 mm and 81 mm mortars and the 105 mm projectile were also conducted at this test range during this time. The

detonations were all initiated by packing the fuze wells with C-4. It was observed that the fragments from the water tests were significantly larger than those from the barricade tests. This is most likely due to the confinement of the water. Compared to the number of fragment impacts observed in the barricade tests, a very small number of fragments penetrated the witness panels in the water tests. The water contained all but the most energetic fragments. A summary of the penetration distances is presented in Table 6. The screen distance is the distance of the first screen that was not penetrated by fragments. The panel distance is the longest travel distance through water of a fragment impacting the witness panel.

Because these fragments were larger than would be expected from the detonation of a munition not submerged in water, they probably penetrated a greater thickness of water than would be expected in an intentional detonation of a munition in the field. Consequently, in actual field conditions, the thickness of water required to contain munition fragments can be expected to be less than those shown here.

TABLE 6 – Water Penetration Distance, Phase One

Munition	Fragment Penetration, in.	
	Screen	Panel
60 mm M49A4	< 10	8.5
81 mm M362A	< 25	14
105 mm M1	< 42	53
155 mm M107	< 70	105

2.2 Phase Two Tests

Phase Two tests were set up in a manner simulating actual field conditions. For each test the munition was placed in a horizontal orientation in a hole with the top of the munition six inches below the ground surface. A piece of plywood was placed over the hole to keep the water containers from resting on the munition. The detonation was initiated using a GOEX oil well perforator charge containing 26 grams of RDX. The perforator was placed on the side of the munition so that the shaped charge was directed slightly downward. Pressure gages and sound meters were used to measure the blast effects. Video cameras and a high speed digital camera were used to record each test. The test setup is shown in Figure 2.

2.2.1 155 mm M107 Projectile

Two water containment systems were tested with the 155 mm M107 projectile. The first system was two layers of 55 gallon drums and the second system was a single 1100 gallon agricultural tank.

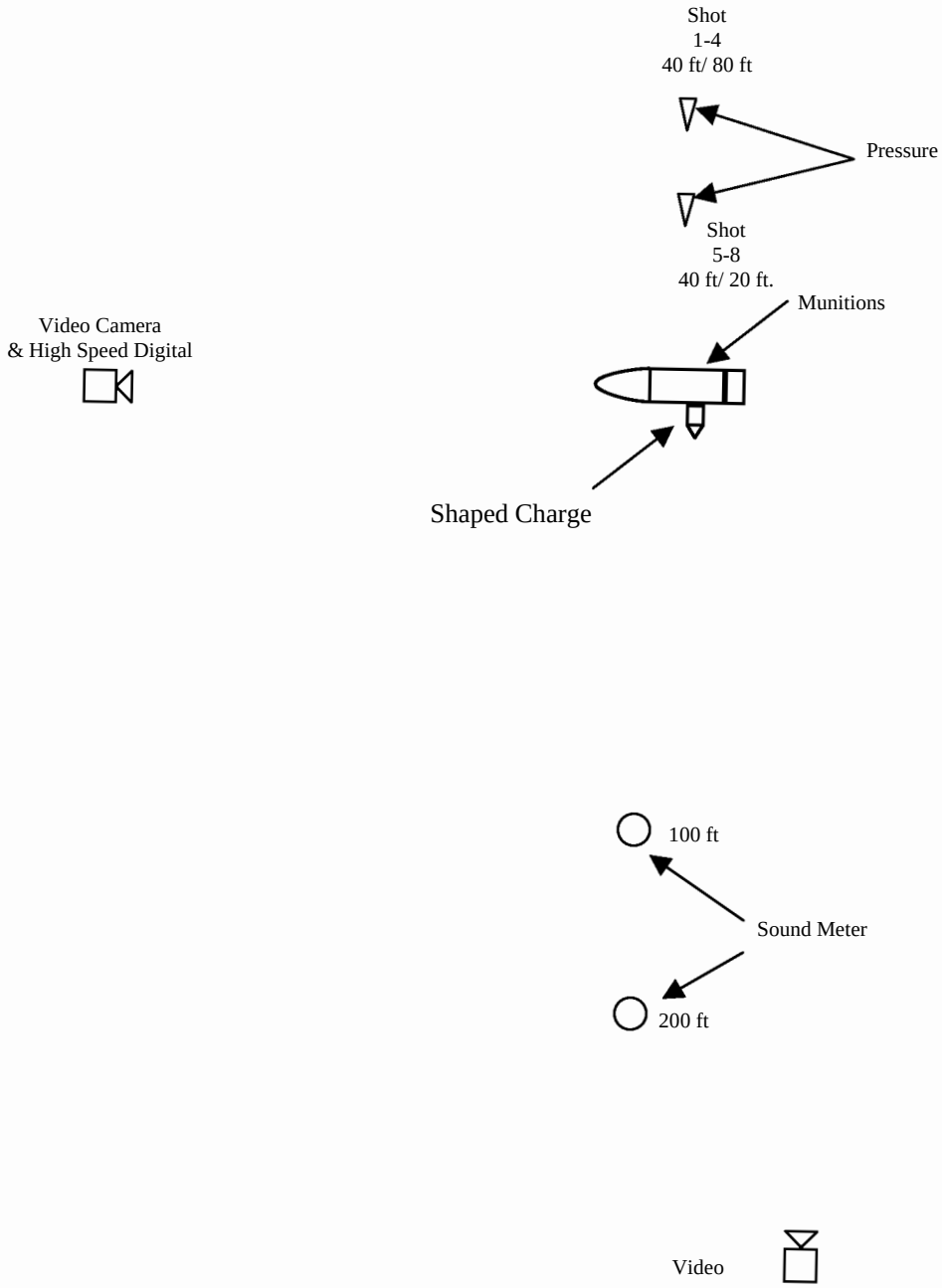


FIGURE 2 – Instrument and Camera Layout for Phase Two Tests

2.2.1.1 Water Contained in 55 Gallon Drums

After placing the 155 mm M107 with the initiator in the hole (see Figure 3), a sheet of ¾ inch plywood was placed over the hole and two layers of 55 gallon drums were placed over the projectile. A total of 28 drums were used with a witness panel placed between the layers and around the outside of the drums. This layout is shown in Figure 4.

The barrels were thrown seventy feet into the air. One barrel, mostly intact, was recovered about 300 feet from ground zero. It had apparently rolled part of this distance. The rest of the barrels were recovered within 100 feet of the crater.

A partially destroyed barrel was recovered approximately 55 feet from the crater with a 3 inch long fragment embedded in the inside surface. Beside this barrel was another fragment about 2 inches long, which may have fallen out of the barrel as it rolled. A small fragment was found inside one of the barrels from the top layer. Several fragments were found between 30 and 40 feet from the crater.

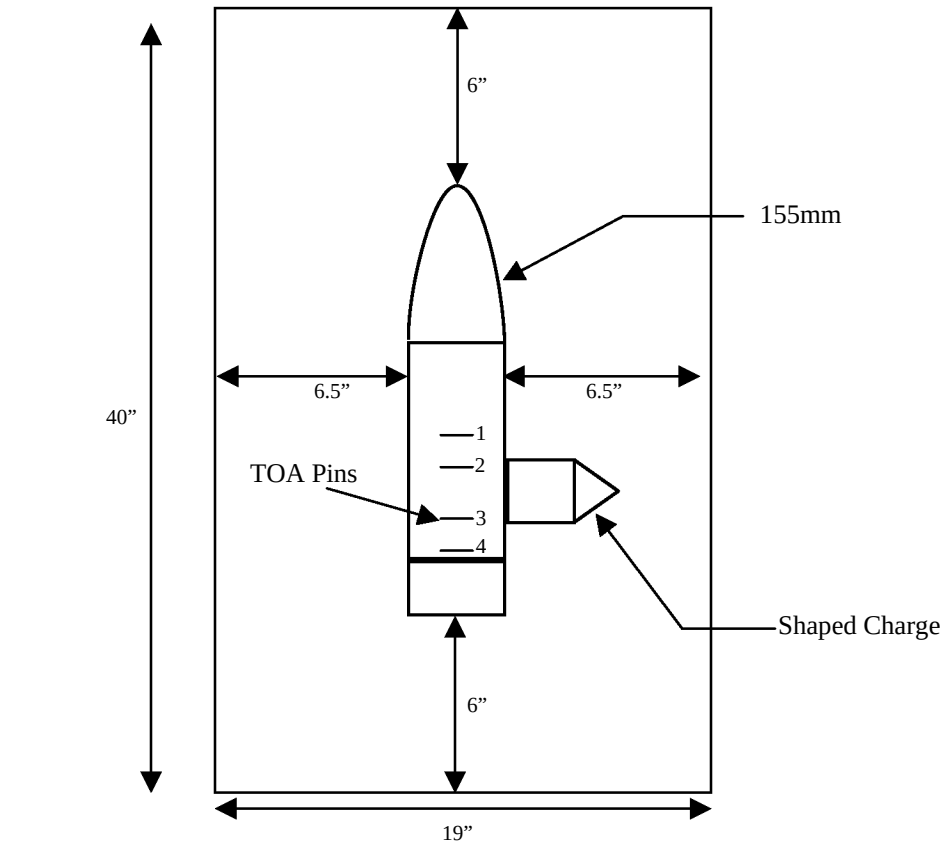
A small fragment hole (about ¼ inch in diameter) was found in the witness plate that was between the layers of barrels. The penetration appeared in the gap between barrels indicating that at least part the fragments path was through air and not water. The top barrel directly over the charge was perforated on the bottom and a circular section over the charge was dented by fragments but not perforated at the top.

Airblast and sound pressure measurements (converted from decibels to psi) are plotted against open-air blast pressure curves for a 155 mm M107 projectile in Figure 5.

Fragments from the 155 mm M107 projectile can penetrate more water than the 3 ft height of the barrels. Because there are significant gaps between the barrels when they are stacked (even more so on uneven ground), a greater area must be covered with barrels to insure that fragments do not escape. This method is very time consuming. Several hours were required to stack and fill all the barrels with water.

2.2.1.2 Water Contained in 1100 Gallon Agricultural Tank

An 1100 gallon agricultural tank was placed over the munition and filled with water. The cylindrical tank was 7 feet in diameter and 58 inches tall. The opaque plastic was approximately 1/8 inch thick. The test layout is shown in Figure 6. The detonation tore the tank into large pieces. One piece was recovered approximately 250 feet from ground zero. One fragment was embedded in the inner side of a piece of the tank but no fragments penetrated the tank.



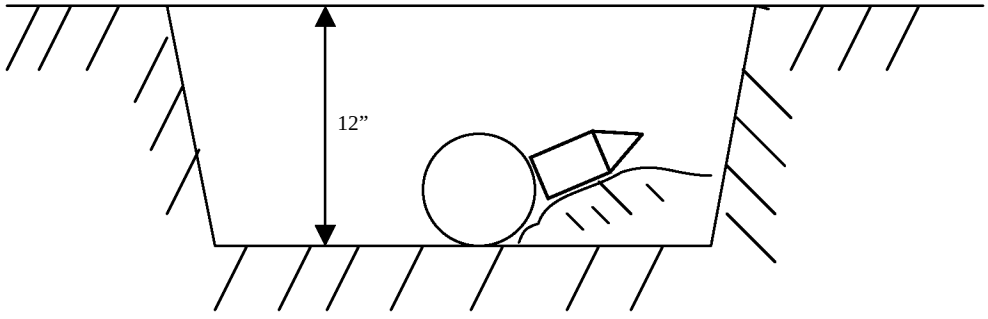


FIGURE 3 – Munition and Initiator Placement for 155 mm M107 Projectiles

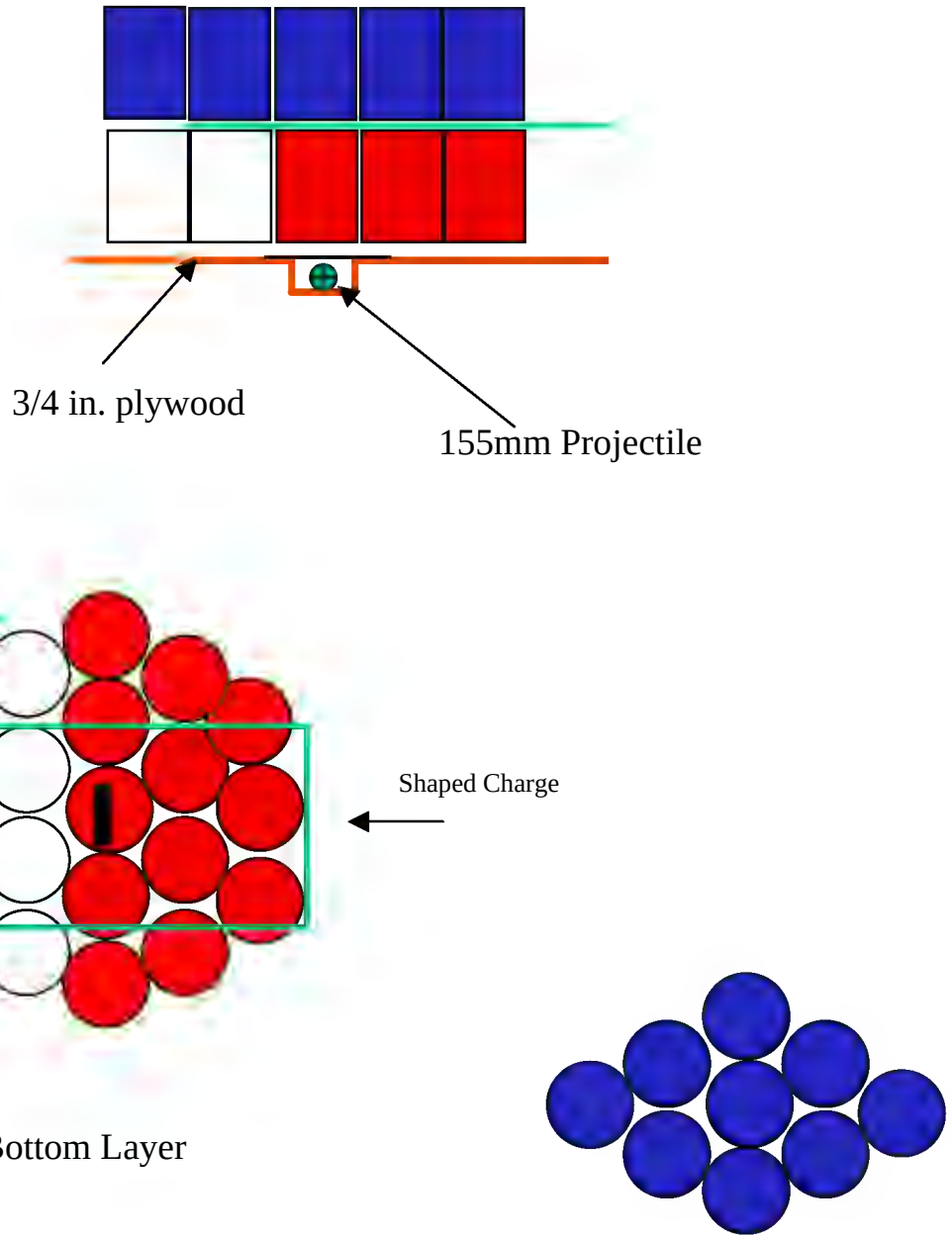


FIGURE 4 – Test Layout for 155 mm M107 Under 55 Gallon Drums

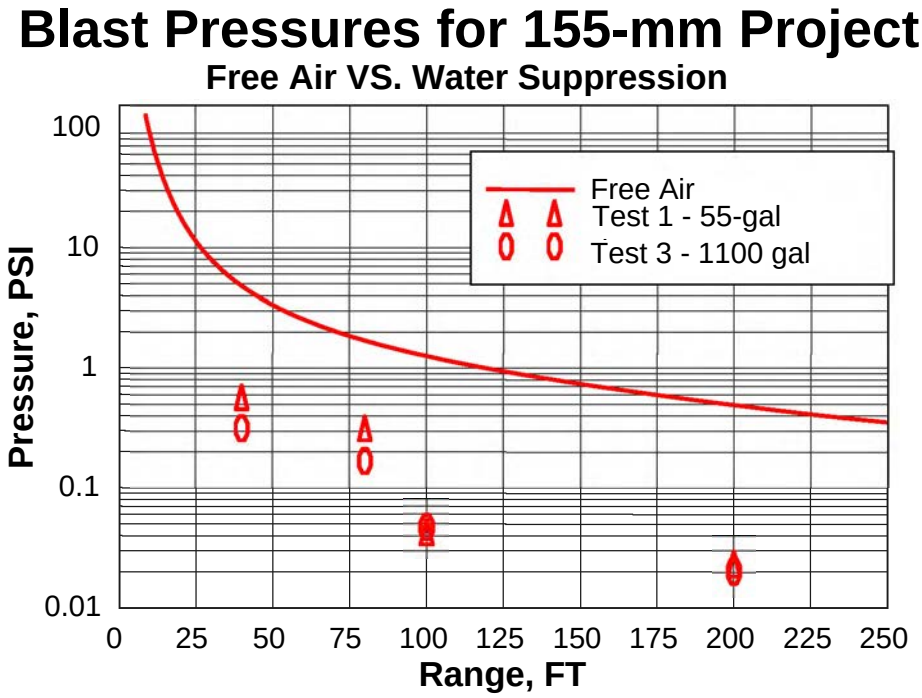


FIGURE 5 – 155 mm M107 Blast Pressures

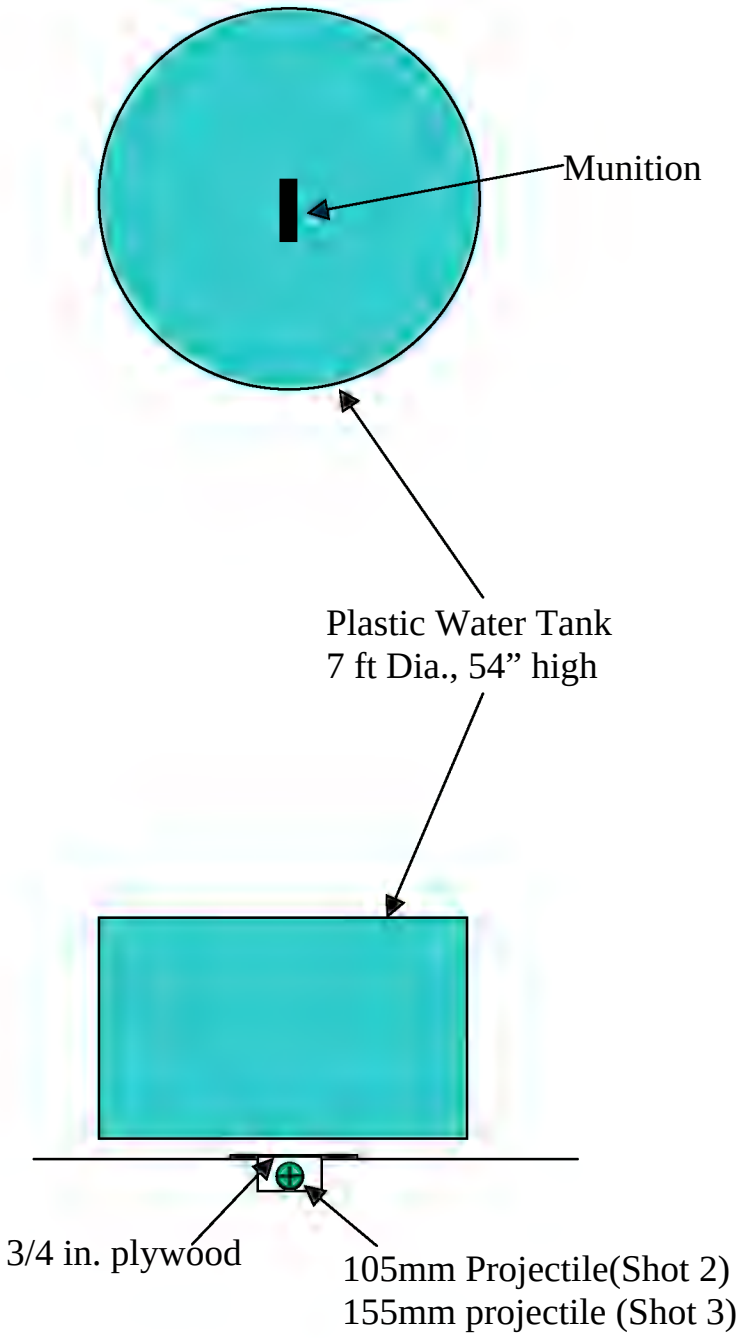


FIGURE 6 – Layout for Tests Using 1100 Gallon Agricultural Tank

2.2.2 105 mm M1 Projectile

Two water containment systems were tested with the 105 mm M1 projectile. The first system was two layers of 55 gallon drums and the second system was a single 1100 gallon agricultural tank.

2.2.2.1 Water Contained in 55 Gallon Drums

After placing the 105 mm M1 with the initiator in the hole (see Figure 7), a sheet of ¾ inch plywood was placed over the hole and two layers of 55 gallon drums were placed over the projectile. A total of 22 drums were used with a witness panel placed between the layers and around the outside of the drums. This layout is shown in Figure 8.

Several fragments penetrated the witness panel between the layers of drums and there were a few dents where the panel was impacted but the fragments did not penetrate. As in the 155 mm M107 test, the fragments penetrating the witness panel were in the gaps between barrels.

The furthest drum was recovered 70 feet from ground zero. Most of the top layer of drums seemed to come straight back down and land in or near the crater. Two of the drums in the crater were undamaged and full of water.

Airblast and sound pressure measurements (converted from decibels to psi) are plotted against open-air blast pressure curves for a 105 mm M1 projectile in Figure 9.

2.2.1.2 Water Contained in 1100 Gallon Agricultural Tank

The test layout is shown in Figure 6. Most debris was within 35 feet of the crater. A number of fragments were found within 50 feet of ground zero, including a piece of the base plate at 50 feet off the base end of the munition. A large piece of the tank was found at 180 feet. A 6 inch long fragment was stuck in the plastic with the bulk of the fragment on the inside of the tank. There were several dents in the witness panels, but only one complete penetration and the fragment causing this penetration was found within a few feet of the panel. Only one obvious exit hole was found in the side of the tank.

The tank is light, easy to place and, because of a large filler hole, can be filled with water in just a few minutes. This container defeated essentially all of the fragments. The one or two that did penetrate the container had been slowed enough that they did not travel any distance. The container pieces traveled further than these primary fragments.

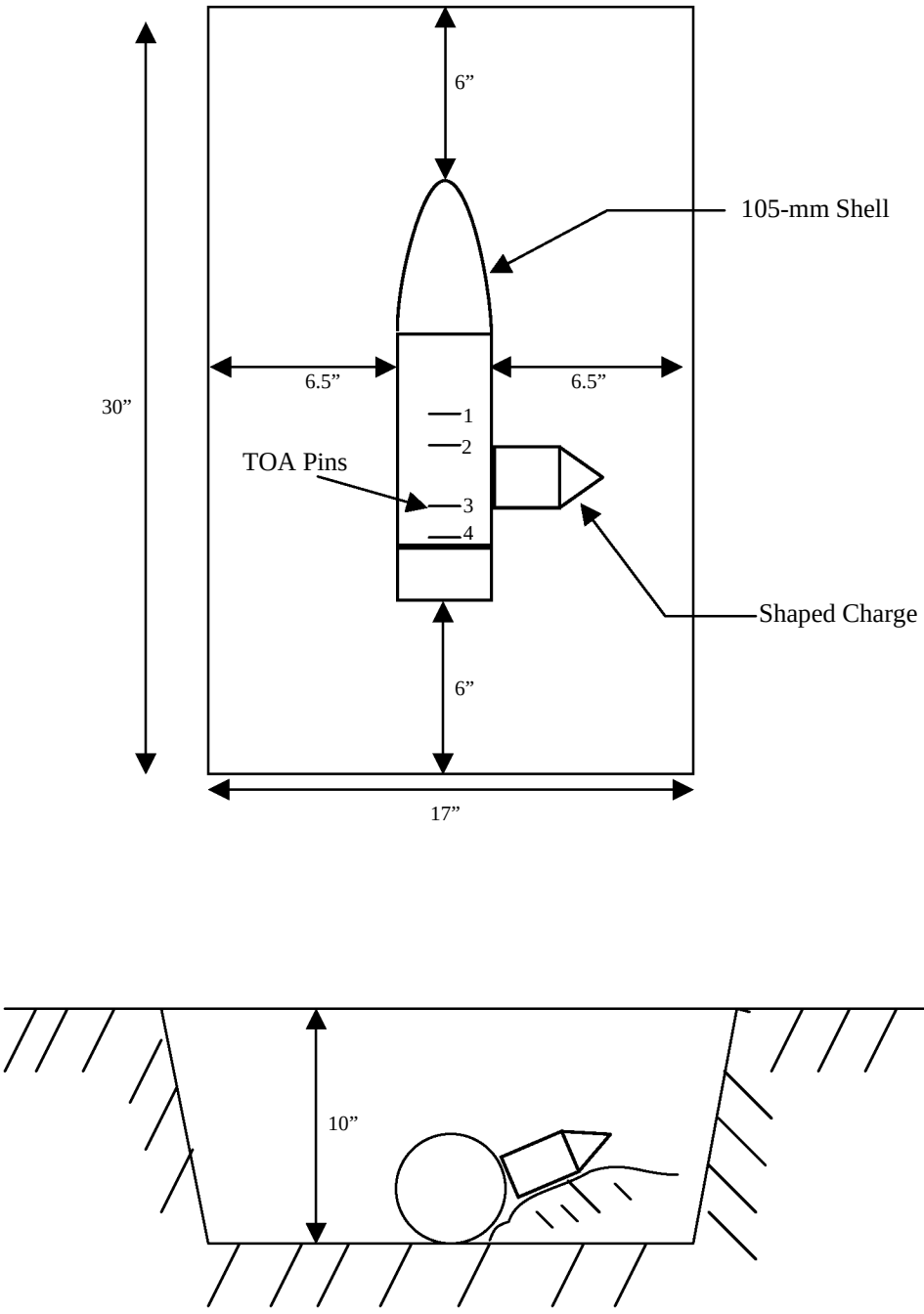


FIGURE 7 – Munition and Initiator Placement for 105 mm M1 Projectiles

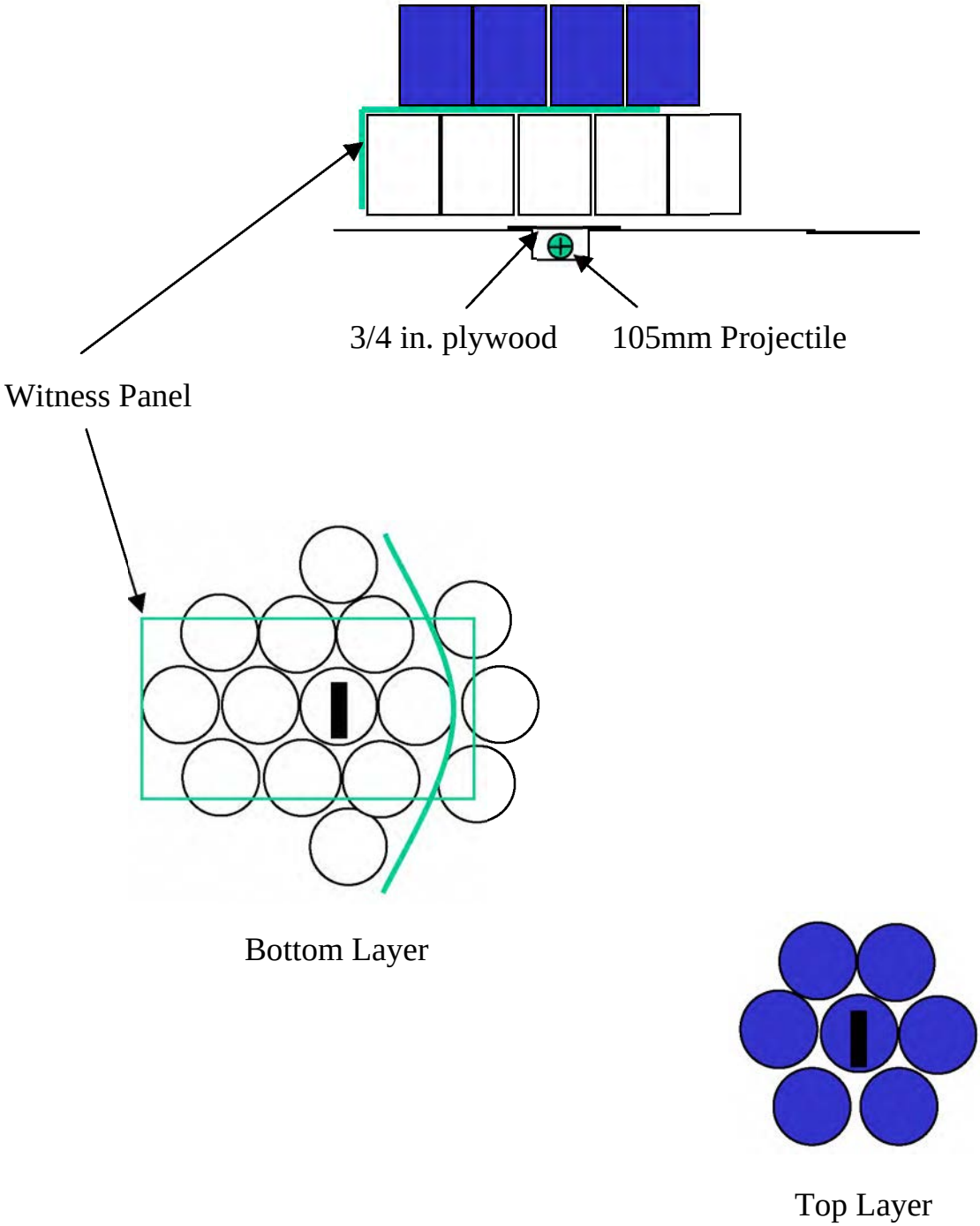


FIGURE 8 - Test Layout for 105 mm M1 Under 55 Gallon Drums

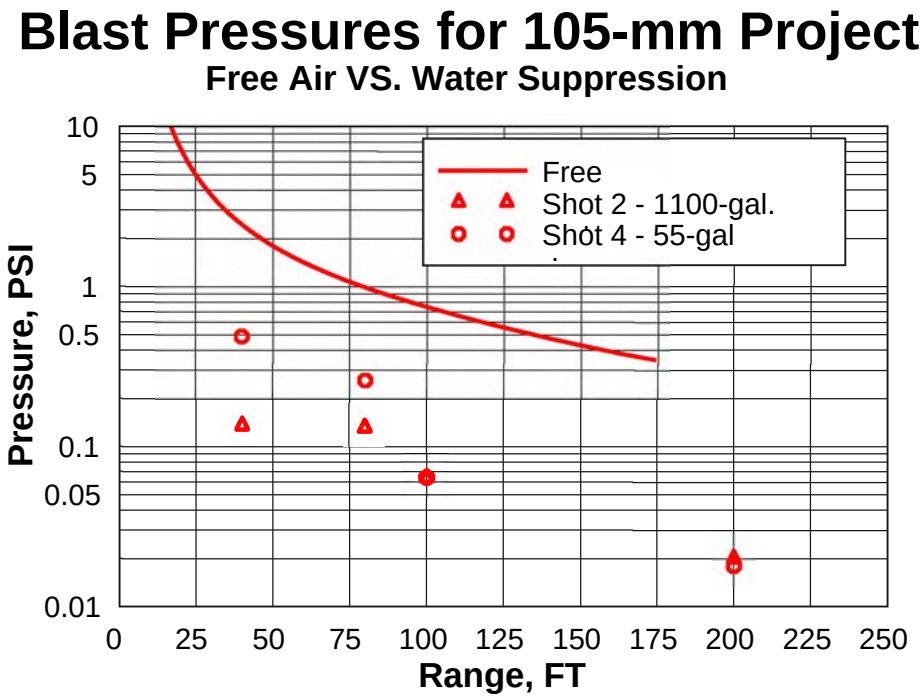


FIGURE 9 - 105 mm M1 Blast Pressures

2.2.3 81 mm M362A Mortar

Two water containment systems were tested with the 81 mm M362A mortar. The first system was two layers of 5 gallon plastic carboys and the second system was a 90 inch diameter inflatable wading pool.

2.2.3.1 Water Contained in 5 Gallon Carboys

After placing the 81 mm M362A with the initiator in the hole (see Figure 10), a half sheet of ¾ inch plywood was placed over the hole and two layers of 5 gallon carboys were placed over the mortar. A total of 31 carboys were used with a witness panel placed between the layers and around the outside of the carboys. This layout is shown in Figure 11.

There was one small fragment hole in the witness panel over the bottom layer of containers and a larger hole about 3 inches long and an inch wide right behind the rear of the munition, probably made by the tail fin. One carboy was found off the side of the stack in the woods at 223 feet and another in a pond about 240 feet off the nose end of the munition. Several were found at distances near 100 feet. Many were still full of water. The tail fin of the mortar was recovered intact directly to the rear of the munition at a distance of 107 feet. Blast pressures from the 81 mm tests are shown in Figure 12.

2.2.3.2 Water Contained in 90 inch Inflatable Wading Pool

After placing the 81 mm M362A with the initiator in the hole, a half sheet of ¾ inch plywood was placed over the hole and a 90 inch diameter inflatable wading pool was placed over the mortar (see Figure 16). The water depth was 18 inches. A witness panel was placed over the pool.

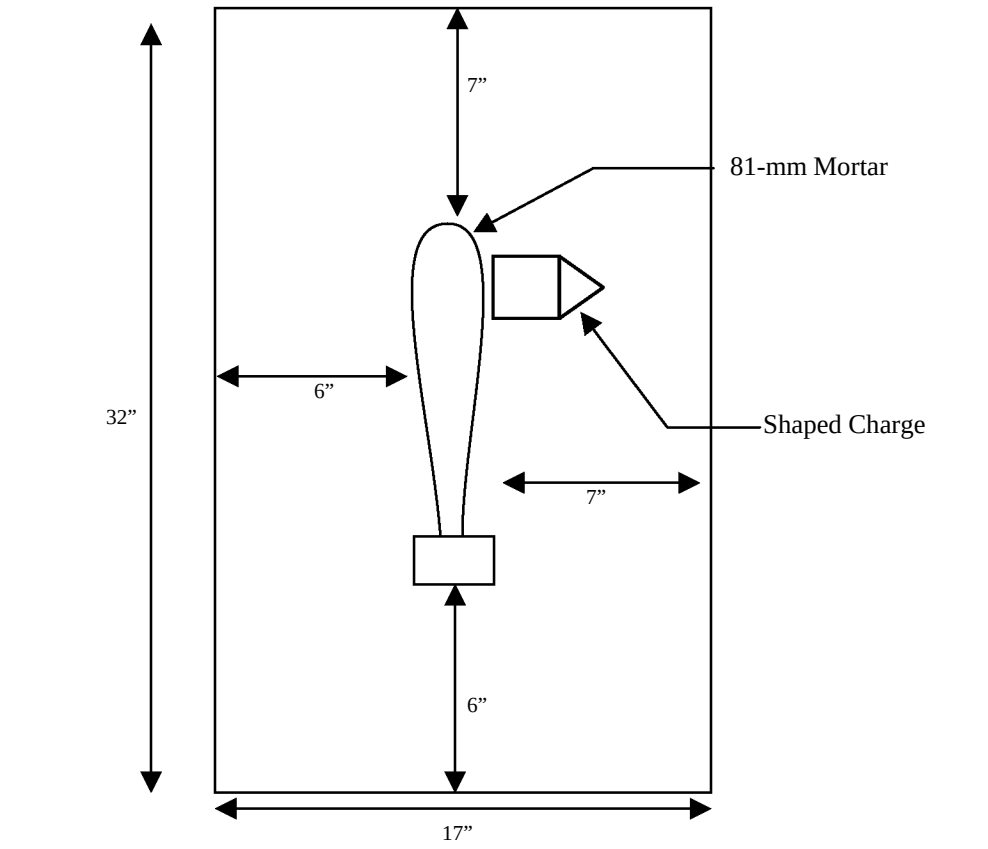
The witness panel was thrown several feet into the air. A hole was blown in the bottom of the pool but the inflated perimeter of the pool was essentially intact. The side of the pool had a small puncture on the inside that caused it to slowly deflate. The witness panel was not perforated.

2.2.4 60 mm M49A4 Mortar

Two water containment systems were tested with the 60 mm M49A4 mortar. The first system was two layers of 5 gallon plastic carboys and the second system was a 90 inch diameter inflatable wading pool.

2.2.4.1 Water Contained in 5 Gallon Carboys

After placing the 60 mm M49A4 with the initiator in the hole (see Figure 13), a half sheet of ¾ inch plywood was placed over the hole and two layers of 5 gallon carboys were placed over the mortar. A total of 11 carboys were used with a



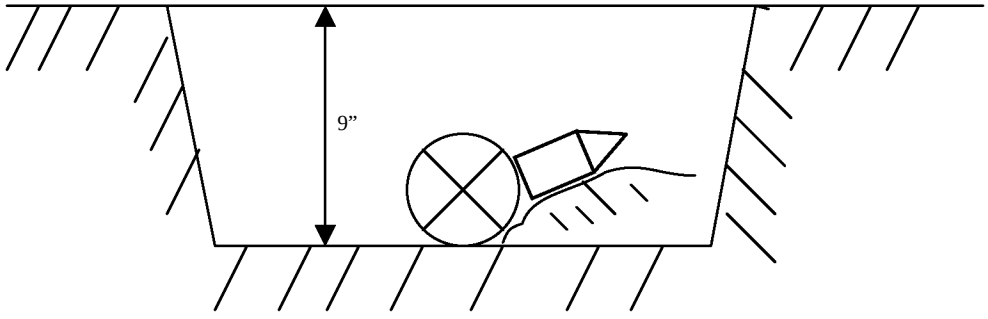


FIGURE 10 – Munition and Initiator Placement for 81 mm M362A Mortars

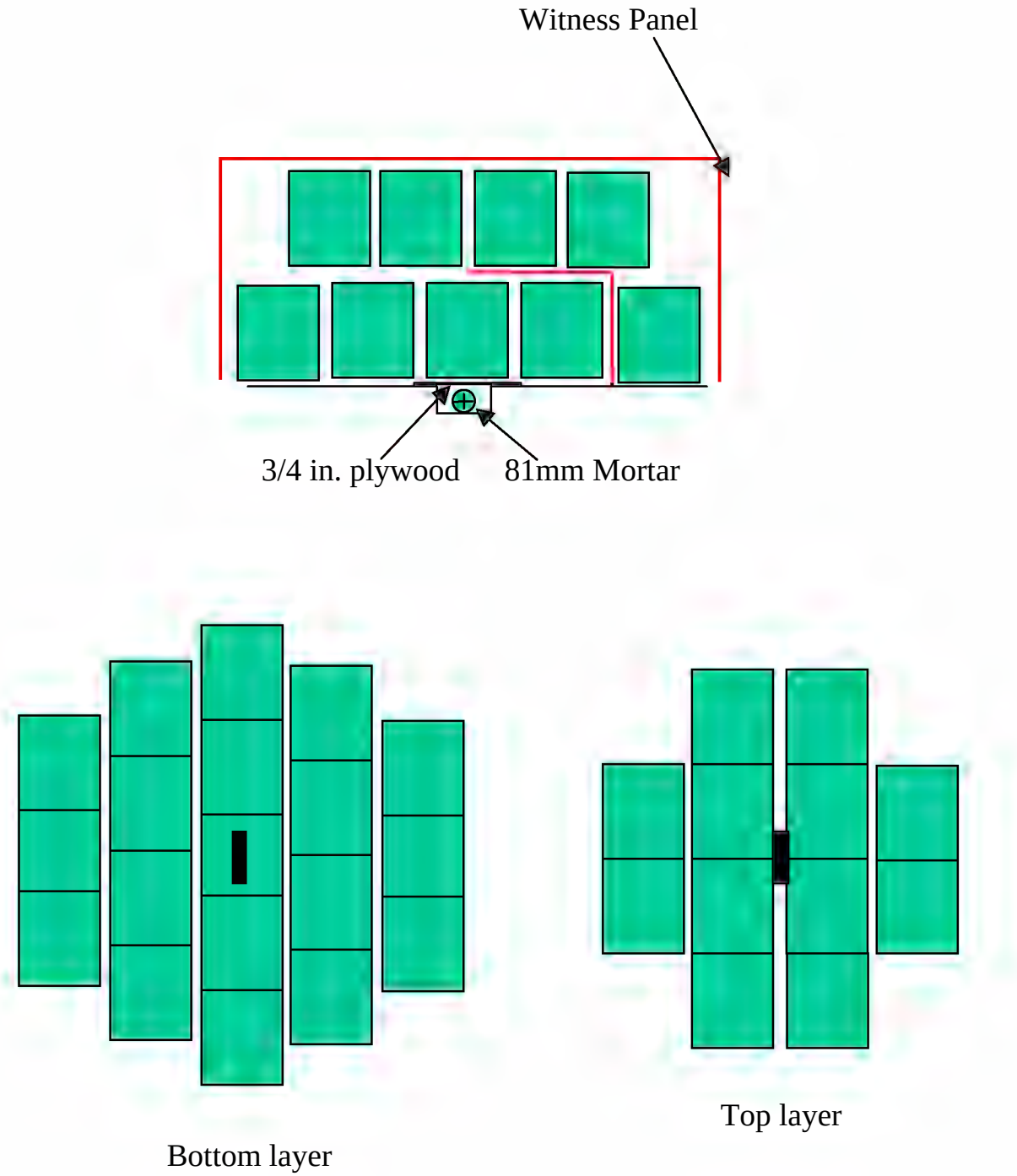


FIGURE 11 - Test Layout for 81 mm M362A Under 5 Gallon Carboys

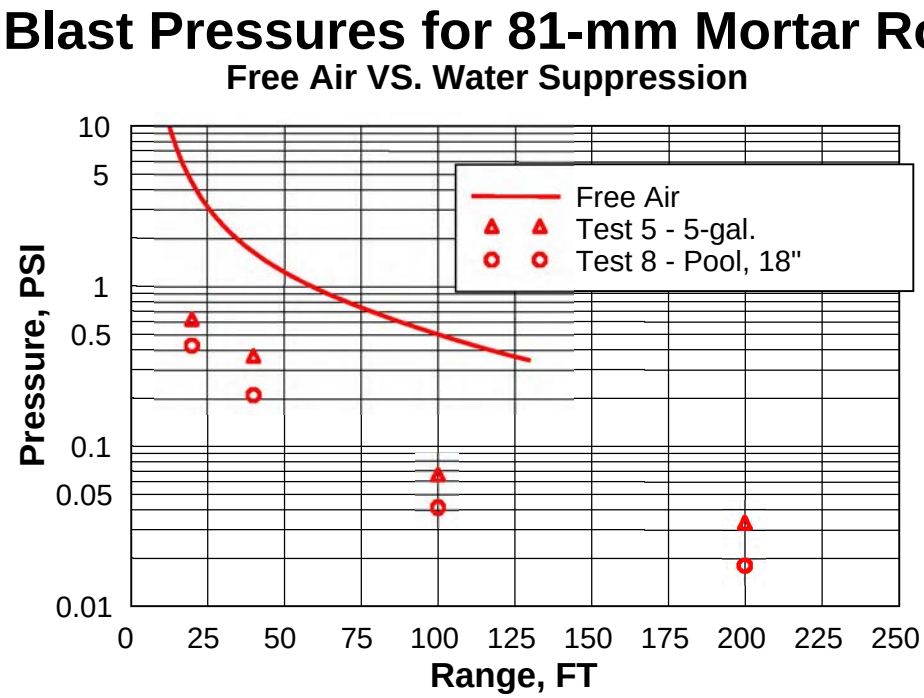


FIGURE 12 - 81 mm M362A Blast Pressures

witness panel placed between the layers and around the outside of the carboys. This layout is shown in Figure 14.

The carboys were thrown more than 100 feet into the air. Those on top landed within 10 feet of the crater. It was observed that the containers on the outer layers are the ones thrown the furthest. The most distant carboy on this test was recovered 44 feet from the nose of the munition. There were no holes in the witness panels. The blast pressures for the 60 mm tests are shown in Figure 15.

2.2.4.2 Water Contained in 90 inch Inflatable Wading Pool

After placing the 60 mm M49A4 with the initiator in the hole, a half sheet of ¾ inch plywood was placed over the hole and a 90 inch diameter inflatable wading pool was placed over the mortar (see Figure 16). The water depth was 18 inches. A witness panel was placed over the pool.

The witness panel was thrown off of the pool. A hole was blown in the bottom of the pool but the inflated perimeter of the pool was not punctured. There were no perforations or even dents in the witness panel.

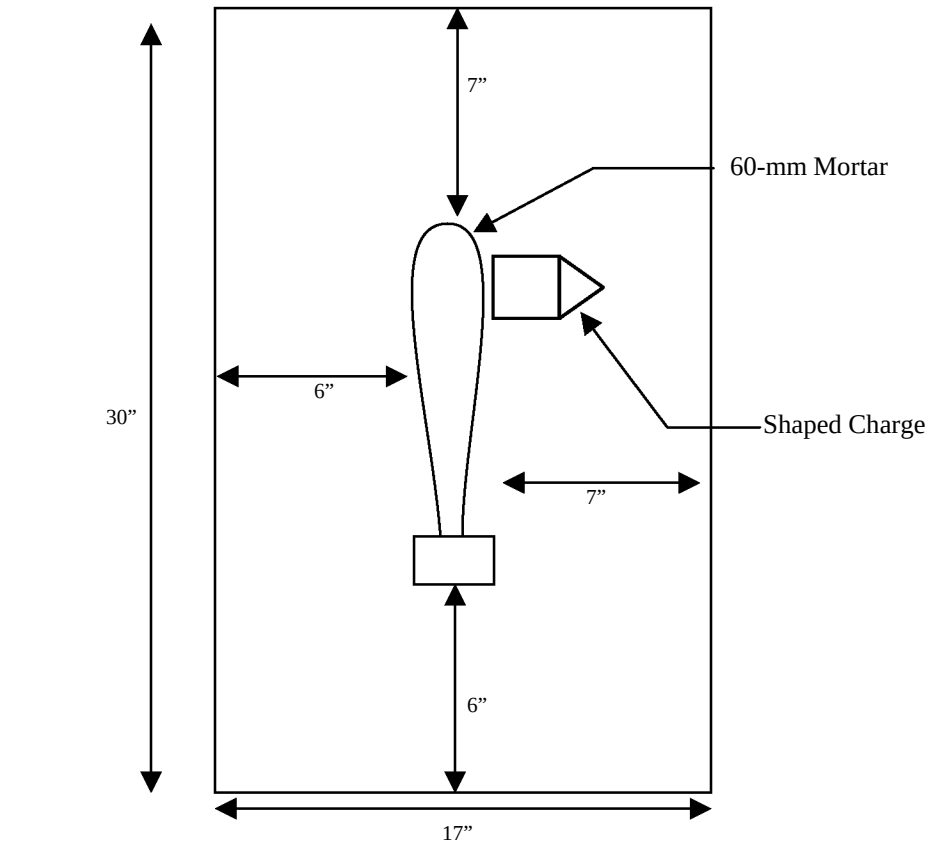
2.2.5 Phase Two Summary and Conclusions

Water is an excellent medium for mitigating blast and fragmentation due to the intentional detonation of unexploded ordnance. Test results show that noise due to detonation is reduced by the water and the fragments from the munitions can be defeated by water.

The best results were obtained using single containers for the water. When multiple containers are used fragments can travel through gaps between containers and the containers are thrown some distance by the blast. Also, containers that are not rigid seem to be a better option than rigid containers because the pieces of the non-rigid containers are smaller, lighter (non-hazardous) and don't travel as far. Non-rigid containers require a more level ground surface but the sides could be supported by soil or sandbags.

As the required thickness of water increases, rigid sides are necessary to contain the large volumes of water and the rigid sides may contribute to the secondary fragment distances. The small pools are readily available at local stores during the spring and early summer but may be difficult to obtain at other times. The agricultural tanks are available any time but may need to be ordered requiring advance planning.

Whenever possible a half sheet (4 ft x 4 ft) of plywood rather than a full sheet (8 ft x 8 ft) should be used under the charge. All of the plywood should be covered by the water container(s) to minimize debris from the plywood.



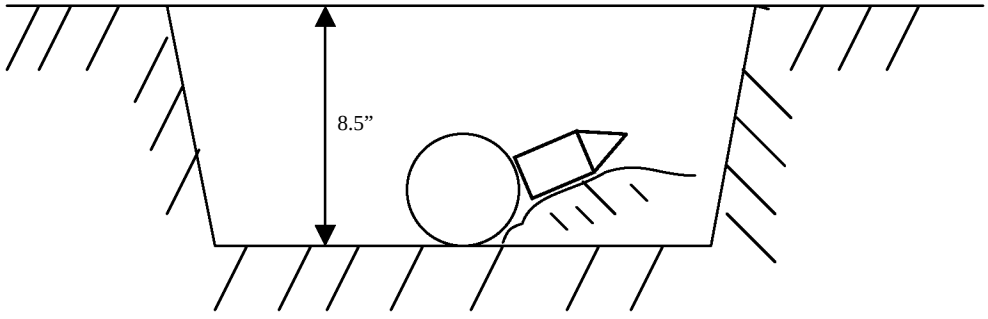
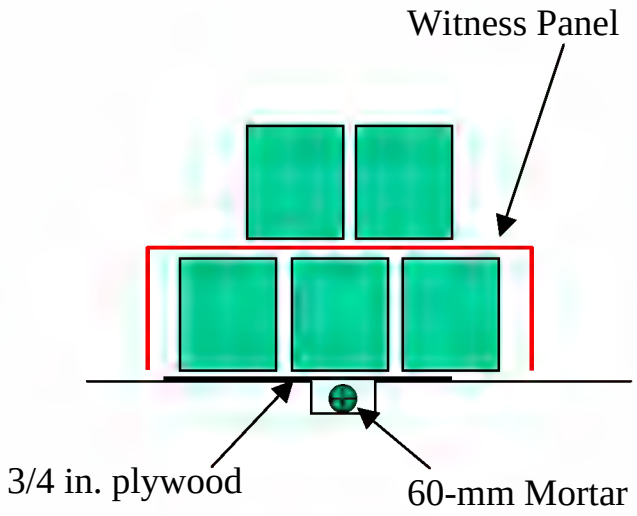
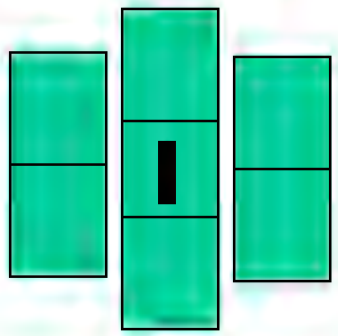
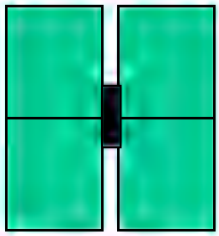


FIGURE 13 – Munition and Initiator Placement for 60 mm M49A4 Mortars





Bottom layer



Top layer

FIGURE 14 - Test Layout for 60 mm M49A4 Under 5 Gallon Carboys

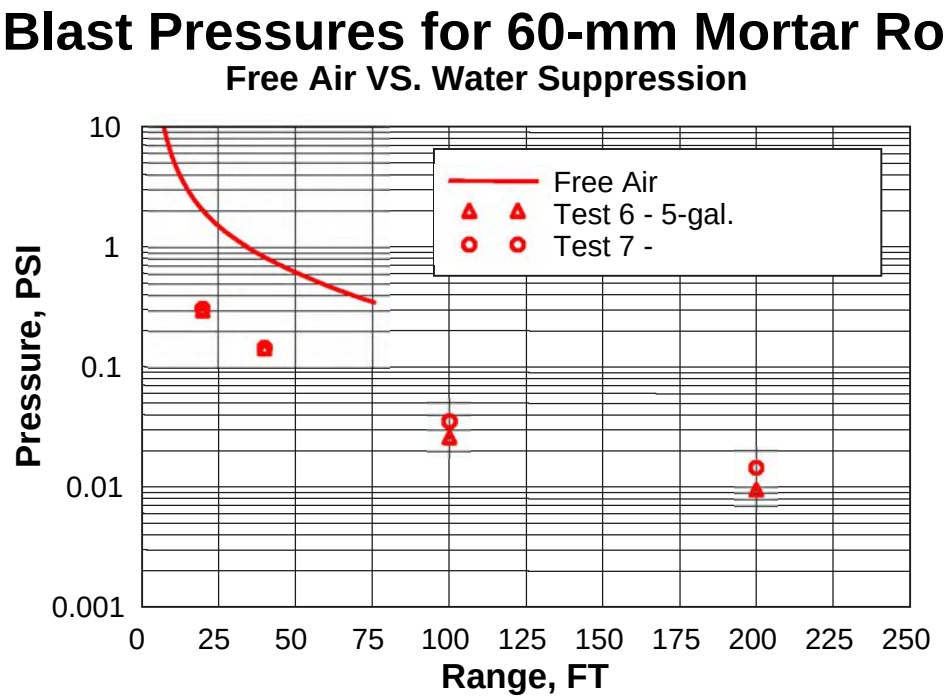


FIGURE 15 - 60 mm M49A4 Blast Pressures

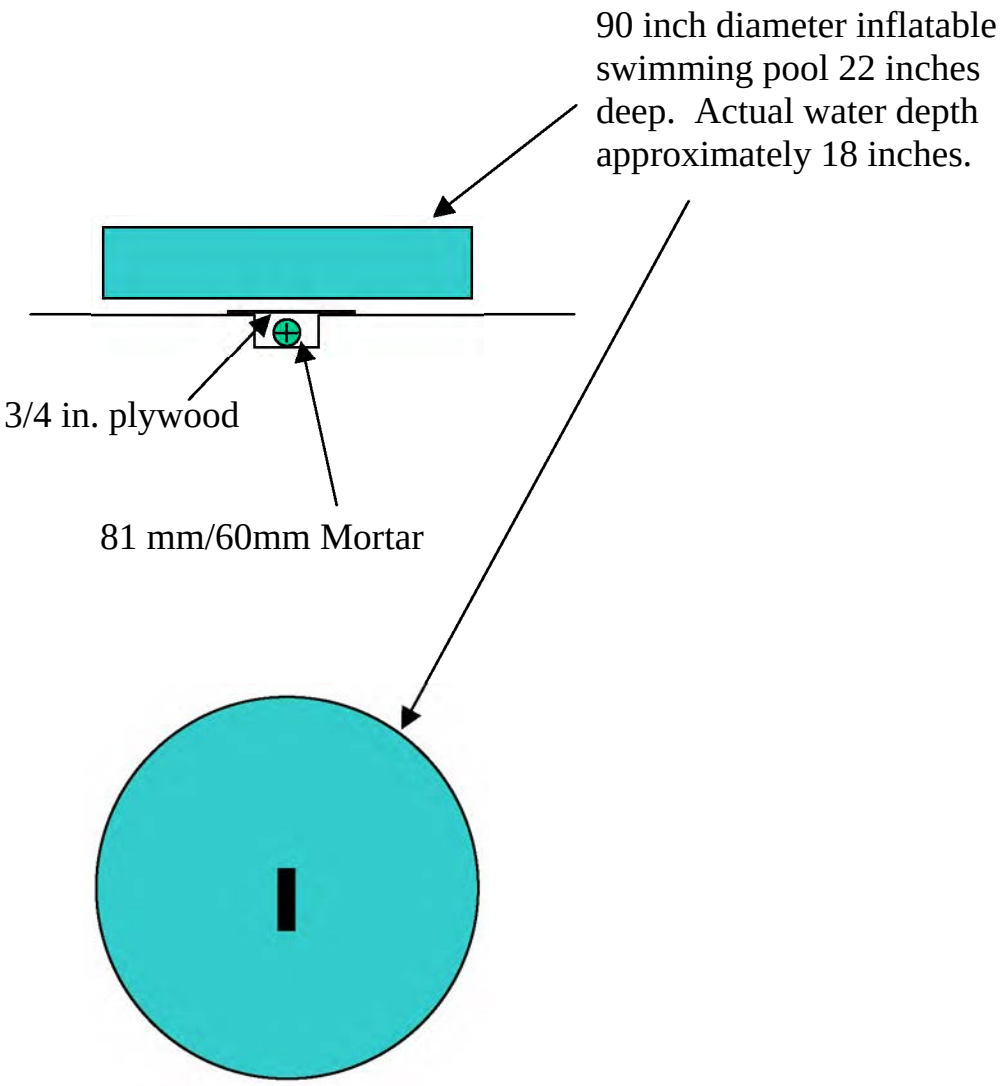


FIGURE 16 - Test Layout for 81 mm M362A and 60 mm M49A4 Under Inflatable Pool

Care should be taken to insure that there are no water spills of sufficient volume to the hole in which the munition is located. This could lead to a misfire. Also, as observed in phase one, the water may cause sufficient confinement to increase fragment size and penetration capabilities.

3.0 Water Mitigation for Intentional Detonations

3.1 Water Containment System

Based on the results from the Phase Two tests, the fragments from an intentional detonation of a 155 mm M107 or a 105 mm M1 projectile are defeated using an 1100 gallon agricultural tank filled with water. The 55 gallon drums are not a viable system for defeating fragments from an intentional detonation because of the gaps between the cylindrical barrels. The fragments from an intentional detonation of an 81 mm M362A or a 60 mm M49A4 mortar are defeated using either a system of 5 gallon plastic carboys or a 90 inch diameter, 18 inch deep wading pool. The results of the Phase Two tests are summarized in Table 7. To be conservative, the maximum secondary debris throw distance shown in Table 7 is 10% greater than the measured maximum secondary debris throw distance. Due to the small values, the overpressures have not been increased from the measured values.

TABLE 7 – Summary of Results From Phase Two Tests

Munition	Water Containment System	Max. Secondary Debris Throw Distance (ft)	Max Peak Overpressure (psi)				
			@ 20 ft	@ 40 ft	@ 80 ft	@ 100 ft[A]	@ 200 ft[A]
155 mm M107	1100 gal. Tank	275		0.28	0.15	0.0415	0.018
105 mm M1	1100 gal. Tank	198		0.136	0.132	0.064	0.02
81 mm M362A	5 gal. Carboys	264	0.61	0.36		0.064	0.0325
81 mm M362A	Inflatable Pool	See note	0.43	0.21		0.0415	0.018
60 mm M49A4	5 gal. Carboys	48	0.29	0.14		0.0251	0.0092
60 mm M49A4	Inflatable Pool	See note	0.31	0.147		0.0352	0.0145

[A]Pressure calculated from measured sound level.
Note: Inflatable pool did not produce any hazardous secondary debris.

The four munition types tested do not cover all of the munitions that may be encountered. To determine the water containment system required for a particular munition other than those tested, the approach is as follows:

(1) Determine the initial fragment velocity (v_f) in ft/s, the maximum fragment weight (W_f) in pounds, and the equivalent weight kinetic energy ($W_f v_f^2/2$) in lb-ft^2/s^2 for the particular munition.

(2) Identify the munition with the next largest kinetic energy from the four tested munitions.

(3) Use the water containment system from Table 7 for the tested munition with the next largest kinetic energy shown.

The maximum fragment weight, the initial fragment velocity, and the resulting kinetic energy for a variety of munitions are provided in Table 8. Table 8 also shows the suitable water containment system for these munitions. The munition/initiator placements and water containment systems are detailed in Figures 3, 6, 7, 10, 11, 13, 14, and 16. The maximum fragment weight and the initial fragment velocity values have been determined with the Mott and Gurney equations, as presented in TM 5-1300 [1] and detailed in HNC-ED-CS-S-98-1 [2]. This procedure should not be used to extrapolate water containment systems for munitions larger than the 155 mm M107 projectile.

3.2 Minimum Separation Distance

A minimum separation distance is required for any detonation. This minimum separation distance applies to everyone, both public and operational personnel. The minimum separation distance is the maximum of the debris throw distance, the distance to an overpressure of 0.065 psi (corresponds to $K328 = 328W^{1/3}$, where W is the net explosive weight), or 200 ft. For all munitions tested the overpressure at 200 ft was substantially less than 0.065 psi. In some cases, the debris throw distance exceeds 200 ft. The minimum separation distances are listed in Table 8.

4.0 Summary and Conclusions

A test program has been performed to determine the effects of water for mitigating fragments and blast effects due to an intentional detonation of a munition. Tests were performed using four different munitions and two water containment systems for each munition.

The results of these tests have been used to develop guidelines for the use of water to mitigate fragments and blast effects due to an intentional detonation of a munition. Methods for determining the required water containment system and the resulting minimum separation distance are detailed in Section 3.0. Figures 3, 6, 7, 10, 11, 13, 14, and 16 show the resulting munition/initiator configuration and water containment systems.

In addition to mitigating the fragments and the overpressure, water quenches the fireball due to an explosion. Therefore, this system insures that there in no fire hazard from an intentional detonation.

5.0 References

1. TM 5-1300, “Structures to Resist the Effects of Accidental Explosions”, Departments of the Army, the Navy, and the Air Force, November 1990.

2. HNC-ED-CS-S-98-1, “Methods for Predicting Primary Fragmentation Characteristics of Cased Explosives”, M. Crull, U.S. Army Engineering and Support Center, Huntsville, January 1998.

TABLE 8 – Water Containment System and Minimum Separation Distance

Munition	Max Fragment Weight (lb)	Critical Fragment Velocity (fps)	Equivalent Weight Kinetic Energy 10^6 (lb-ft^2/s^2)	Water Containment System	Minimum Separation Distance (ft)
20 mm M56A4	0.00058	3183	0.0029503	5 gal carboys/ inflatable pool	200
25 mm M792	0.00820	4256	0.0742528	5 gal carboys/ inflatable pool	200
M31 Rifle Grenade[A]	0.000361	11642	0.0244643	5 gal carboys/ inflatable pool	200
VB Rifle Grenade Mark I	0.0078	3660	0.0522428	5 gal carboys/ inflatable pool	200
37 mm Mk I, LE Practice	0.034207	1368	0.0320079	5 gal carboys/ inflatable pool	200
37 mm MK II	0.02953	5758	0.4894774	5 gal carboys	264
				inflatable pool	200
40 mm M406	0.00036	4508	0.0036986	5 gal carboys/ inflatable pool	200
GP Grenade M42 (submunition)[A]	0.00035	5805	0.0058803	5 gal carboys/ inflatable pool	200
40 mm MK2 Mod 0	0.03306	3605	0.2148275	5 gal carboys/ inflatable pool	200
40 mm HEDP M433	0.00023	11313	0.0147821	5 gal carboys/ inflatable pool	200
M73 Submunition	0.00200	8059	0.0649475	5 gal carboys/ inflatable pool	200
57 mm Chinese	0.01940	5500	0.2933645	5 gal carboys/ inflatable pool	200
57 mm M306	0.01291	3495	0.0788236	5 gal carboys/ inflatable pool	200
MK II Grenade	0.014217	3425	0.0833871	5 gal carboys/ inflatable pool	200
M39 Submunition	0.00011	2338	0.0003006	5 gal carboys/ inflatable pool	200
2.36 " Rocket (Case Only)	0.001035	8888	0.0408807	5 gal carboys/ inflatable pool	200
60 mm M49A3	0.02367	5114	0.3095835	5 gal carboys/ inflatable pool	200
60 mm M49A5	0.01660	6290	0.328382	5 gal carboys/ inflatable pool	200
M15 WP Grenade	0.00340	2685	0.0122557	5 gal carboys/ inflatable pool	200
BLU-59, BLU-26, BLU-36 Submunition	0.00152	6278	0.0299541	5 gal carboys/ inflatable pool	200

TABLE 8 (cont) - Water Containment System and Minimum Separation Distance

Munition	Max Fragment Weight (lb)	Critical Fragment Velocity (fps)	Equivalent Weight Kinetic Energy 10^6 ($lb\text{-}ft^2/s^2$)	Water Containment System	Minimum Separation Distance (ft)
Fragmentation Grenade, M67 (approx)	0.0011828	7006	0.0290283	5 gal carboys/ inflatable pool	200
2.75" M229 Rocket	0.005217	5569	0.0808994	5 gal carboys/ inflatable pool	200
6 lb Incendiary Bomb	0.0021	9431	0.0933909	5 gal carboys/ inflatable pool	200
FMU 54A/B Fuze	0.0064491	9031	0.2629909	5 gal carboys/ inflatable pool	200
75 mm M48	0.15303	3471	0.921814	1100 gal tank	200
3"/50 AP Mk 29	0.42992	1058	0.240619	5 gal carboys/ inflatable pool	200
3 in Stokes Mortar	0.04360	6189	0.835023	1100 gal tank	200
M1A1 Anti-Tank Mine	0.0138139	9891	0.6757199	5 gal carboys	264
				inflatable pool	200
4 lb Frag Bomb M83	0.076176	3266	0.4062754	5 gal carboys	264
				inflatable pool	200
81 mm M374	0.03083	6721	0.6963488	5 gal carboys	264
				inflatable pool	200
81 mm M56	0.03270	5724	0.5356943	5 gal carboys	264
				inflatable pool	200
3.5" M28A2 Rocket Case	0.05242	6126	0.9836056	1100 gal tank	200
90 mm M71	0.3426	2335	0.9339661	1100 gal tank	200
90 mm HEAT M371	0.124	3075	0.5862488	5 gal carboys	264
				inflatable pool	200
20 lb Frag Bomb M41	0.33321	3303	1.8176287	1100 gal tank	275
4 in Stokes Mortar	0.07820	6336	1.5696915	1100 gal tank	200
105 mm M1	0.20573	4055	1.6914479	1100 gal tank	200
105 mm HEAT M456	0.07010	6326	1.4026406	1100 gal tank	200
106 mm M344 (Case)	0.0630543	6238	1.2268048	1100 gal tank	200
4.2 in M3A1	0.07869	6391	1.6069785	1100 gal tank	200
British Naval 4.5"	0.408519	2461	1.237102	1100 gal tank	200
4.5 inch rocket M8	0.1485	5352	2.1268099	1100 gal tank	275
4.7 in Mark I	0.59147	3566	3.7606709	1100 gal tank	275
120mm M356	0.32909	3493	2.0076278	1100 gal tank	275
5 in 38 Caliber Mk 35	0.36485	3563	2.3158861	1100 gal tank	275
6" Trench Mortar	0.11418	3939	0.8857615	1100 gal tank	200
155 mm M107	0.64821	3426	3.8041893	1100 gal tank	275

[A]These rounds contain a shaped charge. Care must be taken that the destruction method does not allow formation of a jet and fragment slug.

APPENDIX

TEST PHOTOGRAPHS

(This is an abridged version of the publication. For the complete version, see the USACE Subfolder provided by UXOSM)

Figure A-1 – Phase 1, 60 mm Test Set-up

Figure A-2 – Phase 1, 60 mm Test, Post Detonation

Figure A-3 – Phase 1, 81 mm Suspended in Pool

Figure A-4 – Phase 1, 81 mm Test Set-up

Figure A-14 – Phase 2, 105 mm Under 1100 Gallon Tank Test Set-up

Figure A-20 – Phase 2, 105 mm Under 55 Gallon Drums Test Set-up

Figure A-22 – Phase 2, 81 mm Under 5 Gallon Carboys Test Set-up

ATTACHMENT 5

WEAPON SPECIFIC FRAGMENTATION CHARACTERIZATION (DDESB TP 16)

APPENDIX B
WEAPON SPECIFIC
FRAGMENTATION CHARACTERIZATION

Table B-1. High Explosive Bombs And Projectiles

Munition	Explosive Weight (lbs) *(kg)*	Diameter (in) *(mm)*	Maximum Fragment Weight (lbs) *(g)*	Fragment Initial Velocity (ft/s) *(m/s)*	Maximum Fragment Range		Hazardous Fragment Distance (ft) *(m)*
					Horizontal (ft) *(m)*	Vertical (ft) *(m)*	
2000 lb Bomb M66A2	1,146.00 *519.814*	23.29 *591.57*	0.9717 *440.7534*	8,316 *2,534.7*	3,607 *1,099.4*	2,855 *870.2*	985 *300.2*
Bomb MK 84	945.00 *428.643*	17.96 *456.18*	2.1766 *987.3025*	4,180 *1,274.1*	3,882 *1183.2*	3,051 *929.9*	925 *281.9*
Bomb BLU - 109	535.00 *242.671*	15.05 *382.27*	3.8517 *1,747.0926*	5,340 *1,627.6*	4,887 *1,489.6*	3,760 *1,146.0*	881 *268.5*
GP Bomb (Mk XIII Mod 2)	511.00 *231.784*	17.70 *449.58*	0.9848 *446.6954*	8,239 *2,511.2*	3,617 *1,102.5*	2,859 *871.4*	734 *223.7*
Bomb MK 83	445.00 *201.848*	13.94 *354.08*	0.8923 *404.7433*	6,074 *1,851.4*	3,288 *1,002.2*	2,568 *782.7*	813 *247.8*
Bomb BLU - 110	385.00 *174.632*	13.94 *354.08*	1.0656 *483.3455*	5,463 *1,665.1*	3,382 *1,030.8*	2,625 *800.1*	785 *239.3*
Bomb M64A1	274.00 *124.284*	14.20 *360.68*	0.0221 *10.0334*	8,116 *2,473.8*	2,501 *762.3*	1,991 *606.9*	680 *207.3*
Bomb MK 82 Mod 1	192.00 *87.089*	10.75 *273.05*	0.8963 *406.5300*	5,193 *1,582.8*	3,177 *968.3*	2,462 *750.4*	688 *209.7*
16" Mk 14 Projectile	153.57 *69.658*	16.00 *406.40*	15.4582 *7,011.6759*	2,426 *739.4*	5,639 *1,718.8*	3,995 *1,217.7*	550 *167.6*
250 lb Bomb M 57--TNT	129.02 *58.522*	10.36 *263.14*	0.2894 *131.2572*	8,293 *2,527.7*	2,032 *619.4*	1,625 *495.3*	534 *162.8*
250 lb Bomb M 57--Amatol	113.72 *51.582*	10.36 *263.14*	0.3396 *154.0578*	6,365 *1,940.1*	2,497 *761.1*	1,965 *598.9*	492 *150.0*
Bomb MK 81 Mod 1	100.00 *45.359*	9.00 *228.60*	0.5167 *234.3631*	6,674 *2,034.2*	2,856 *870.5*	2,247 *684.9*	583 *177.7*
100 lb Bomb GP Mk 1	65.00 *29.483*	7.90 *200.66*	0.1013 *45.9487*	9,005 *2,744.7*	1,863 *567.8*	1,491 *454.5*	200 *61.0*
100 lb Bomb AN-M30A1	62.00 *28.123*	8.20 *208.28*	0.0997 *45.2229*	8,414 *2,564.6*	1,831 *558.1*	1,467 *447.1*	483 *147.2*
8 in M106	38.80 *17.599*	8.00 *203.20*	1.6931 *767.9790*	3,091 *942.1*	3,287 *1,001.9*	2,440 *743.7*	530 *161.5*
165 mm M123 Series	34.22 *15.522*	6.50 *165.00*	0.1642 *74.4849*	5,179 *1,578.6*	1,927 *587.3*	1,509 *459.9*	338 *103.0*
175 mm M437 Series	32.00 *14.515*	6.89 *175.00*	0.6378 *289.2997*	4,086 *1,245.4*	2,703 *823.9*	2,068 *630.3*	527 *160.6*
155 mm M795	28.80 *13.063*	6.10 *155.00*	0.5620 *254.9176*	4,635 *1,412.7*	2,699 *822.7*	2,078 *633.4*	436 *132.9*
8 in M650	26.00 *11.793*	8.00 *203.20*	1.3900 *630.4901*	4,035 *1,229.9*	3,201 *975.7*	2,436 *742.5*	397 *121.0*
50 lb Demo Bomb Mk1	25.00 *11.340*	6.10 *154.94*	0.1102 *49.9856*	6,988 *2,129.9*	1,821 *555.0*	1,447 *441.0*	354 *107.9*
155 mm M107	15.45 *7.007*	6.10 *155.00*	0.6482 *294.0227*	3,426 *1,044.2*	2,577 *785.5*	1,983 *604.4*	447 *136.2*
155 mm Mk I	15.17 *6.881*	6.10 *155.00*	0.7681 *348.4206*	4,032 *1,229.0*	2,842 *866.2*	2,169 *661.1*	395 *120.4*
6 in 47 Caliber HC Mk 34	13.22 *5.996*	6.00 *152.40*	0.8196 *371.7397*	3,001 *914.7*	2,510 *765.0*	1,871 *570.3*	403 *122.8*
6" Trench Mortar	13.00 *5.897*	6.00 *152.40*	0.1142 *51.7891*	3,939 *1,200.6*	2,631 *801.9*	2,008 *612.0*	366 *111.6*

Table B-1. High Explosive Bombs And Projectiles (continued)

Munition	Explosive Weight (lbs) *(kg)*	Diameter (in) *(mm)*	Maximum Fragment Weight (lbs) *(g)*	Fragment Initial Velocity (ft/s) *(m/s)*	Maximum Fragment Range Horizontal (ft) *(m)*	Maximum Fragment Range Vertical (ft) *(m)*	Hazardous Fragment Distance (ft) *(m)*
4.5 inch rocket M8	10.80 *4.899*	4.50 *114.30*	0.1485 *67.3581*	5,352 *1,631.3*	1,883 *573.9*	1,478 *450.5*	361 *110.0*
152 mm HE-T M657	9.50 *4.309*	5.98 *151.89*	0.6753 *306.3093*	4,429 *1,350.0*	2,667 *812.9*	2,055 *626.4*	315 *96.0*
4.2 in M3A1	8.17 *3.706*	4.20 *106.68*	0.0787 *35.6916*	6,391 *1,948.0*	1,617 *492.9*	1,284 *391.4*	311 *94.8*
4 in Stokes	7.92 *3.592*	4.00 *101.60*	0.0782 *35.4713*	6,336 *1,931.2*	1,611 *491.0*	1,278 *389.5*	313 *95.4*
5 in 38 Caliber MK 35	7.86 *3.565*	5.00 *127.00*	0.3649 *165.4928*	3,563 *1,086.0*	2,207 *672.7*	1,676 *510.8*	299 *91.1*
120 mm M356	7.84 *3.556*	4.72 *120.00*	0.3291 *149.2724*	3,493 *1,064.7*	2,129 *648.9*	1,616 *492.6*	384 *117.0*
5 in 54 Caliber MK 41	7.59 *3.443*	5.00 *127.00*	0.6726 *305.0846*	2,513 *766.0*	2,370 *722.4*	1,741 *530.7*	358 *109.1*
4.5in Barrage Rocket Mk3	6.50 *2.948*	4.50 *114.30*	0.1043 *47.3280*	6,386 *1,946.5*	1,759 *536.1*	1,394 *424.9*	290 *88.4*
4.7 in Mark I	6.07 *2.753*	4.70 *119.38*	0.5915 *268.2848*	3,566 *1,086.9*	2,540 *774.2*	1,922 *585.8*	319 *97.2*
British Naval 4.5 inch	5.633 *2.555*	4.50 *114.30*	0.4085 *185.3001*	2,461 *750.1*	2,045 *623.3*	1,543 *470.3*	356 *108.5*
105 mm M1	5.07 *2.300*	4.13 *105.00*	0.2057 *93.3191*	4,055 *1,236.0*	1,939 *591.0*	1,494 *455.4*	341 *103.9*
2.75" M229 Rocket	4.80 *2.177*	2.75 *69.85*	0.0052 *2.3664*	5,569 *1,697.4*	1,374 *418.8*	1,088 *331.6*	302 *92.0*
81 mm M56	4.30 *1.950*	3.19 *81.00*	0.0327 *14.8324*	5,724 *1,744.7*	1,216 *370.6*	966 *294.4*	221 *67.4*
Dragon-2 Mk1 (Case Only)	3.80 *1.724*	4.80 *121.92*	0.0046 *2.0865*	10,681 *3,255.6*	395 *120.4*	325 *99.1*	200 *61.0*
44 mm Panzerfaust	3.40 *1.542*	1.73 *43.94*	0.0006 *0.2676*	10,374 *3,162.0*	403 *122.8*	313 *95.4*	200 *61.0*
106 mm M344 (Case)	2.79 *1.266*	4.17 *106.00*	0.0631 *28.6008*	6,238 *1,901.3*	1,506 *459.0*	1,196 *364.5*	N/C *N/C*
20 lb Frag Bomb M41	2.70 *1.225*	3.64 *92.46*	0.3332 *151.1407*	3,303 *1,006.8*	2,103 *641.0*	1,588 *484.0*	275 *83.8*
105 mm HEAT M456	2.140 *0.971*	4.13 *105.00*	0.0701 *31.7967*	6,326 *1,928.2*	1,559 *475.2*	1,233 *375.8*	235 *71.6*
3 in Stokes	2.10 *0.953*	3.00 *76.20*	0.0436 *19.7766*	6,189 *1,886.4*	1,346 *410.3*	1,071 *326.4*	219 *66.8*
81mm M362A1	2.10 *0.953*	3.19 *81.00*	0.0384 *17.4174*	6,252 *1905.6*	1,299 *395.9*	1,034 *315.2*	243 *74.1*
81 mm M374	2.09 *0.948*	3.19 *81.00*	0.0308 *13.9847*	6,721 *2,048.6*	1,233 *375.8*	986 *300.5*	234 *71.3*
90 mm M71	1.975 *0.896*	3.54 *90.00*	0.3426 *155.3999*	2,335 *711.7*	1,955 *595.9*	1,518 *462.7*	250 *76.2*
3.5" M28A2 Rocket Case	1.88 *0.853*	3.50 *88.90*	0.0524 *23.7772*	6,126 *1,867.2*	1,420 *432.8*	1,128 *343.8*	235 *71.6*
90 mm HEAT M371A1	1.72 *0.780*	3.54 *90.00*	0.2081 *94.3921*	3,214 *979.6*	1,724 *525.5*	1,328 *404.8*	231 *70.4*

Table B-1. High Explosive Bombs And Projectiles (continued)

Munition	Explosive Weight (lbs) *(kg)*	Diameter (in) *(mm)*	Maximum Fragment Weight (lbs) *(g)*	Fragment Initial Velocity (ft/s) *(m/s)*	Maximum Fragment Range		Hazardous Fragment Distance (ft) *(m)*
					Horizontal (ft) *(m)*	Vertical (ft) *(m)*	
75 mm Mk I	1.64	2.95	0.1531	3,479	1,702	1,298	238
	0.744	*75.00*	*69.4288*	*1,060.4*	*518.8*	*395.6*	*72.5*
75 mm M48	1.47	2.95	0.1530	3,471	1,701	1,297	234
	0.667	*75.00*	*69.4109*	*1,058.0*	*518.5*	*395.3*	*71.3*
76 mm M352	1.46	2.99	0.2295	2,507	1,742	1,291	253
	0.662	*76.00*	*104.0989*	*764.1*	*531.0*	*393.5*	*77.1*
81 mm M43	1.29	3.19	0.0573	4,933	1,395	1,097	230
	0.585	*81.00*	*25.9907*	*1,503.6*	*425.2*	*334.4*	*70.1*
90 mm HEAT M371 & M431	1.20	3.54	0.1240	3,075	1,546	1,170	209
	0.544	*90.00*	*56.2452*	*937.3*	*471.2*	*356.6*	*63.7*
60 mm M49A5	0.79	2.36	0.0166	6,290	1,013	806	200
	0.358	*60.00*	*7.5296*	*1,917.2*	*308.8*	*245.7*	*61.0*
66 mm M72A2 (LAW) Rocket (Case Only)	0.67	2.60	0.0008	10,015	437	358	200
	0.304	*66.00*	*0.3629*	*3,052.6*	*133.2*	*109.1*	*61.0*
57 mm M306	0.55	2.24	0.0129	3,495	1,073	828	200
	0.249	*57.00*	*5.8540*	*1,065.3*	*327.1*	*252.4*	*61.0*
57 mm Chinese	0.51	2.24	0.0194	5,500	1,032	821	200
	0.231	*57.00*	*8.7978*	*1,676.4*	*314.6*	*250.2*	*61.0*
2.36 " Rocket (Case Only)	0.50	2.36	0.0010	8,888	809	645	200
	0.227	*59.94*	*0.4695*	*2,709.1*	*246.6*	*196.6*	*61.0*
4 lb Frag Bomb M83	0.50	3.12	0.0762	3,266	1,363	1,040	209
	0.227	*79.25*	*34.5527*	*995.5*	*415.4*	*317.0*	*63.7*
60 mm M49A3	0.42	2.36	0.0237	5,114	1,080	856	200
	0.191	*60.00*	*10.7387*	*1,558.7*	*329.2*	*260.9*	*61.0*
40 mm MK2	0.187	1.57	0.0331	3,605	1,095	847	200
	0.085	*40.00*	*14.9959*	*1,098.8*	*333.8*	*258.2*	*61.0*
3"/50 AP Mk 29	0.14	3.00	0.4299	1,058	1,595	1,117	200
	0.064	*76.20*	*195.0079*	*322.5*	*486.2*	*340.5*	*61.0*
25 mm M792	0.096	0.98	0.0082	4,256	756	597	200
	0.043	*25.00*	*3.7188*	*1,297.2*	*230.4*	*182.0*	*61.0*
37 mm MK II	0.053	1.46	0.0245	3,302	980	754	200
	0.024	*37.00*	*11.1130*	*1,006.4*	*299*	*230*	*61*
20 mm M56A4	0.026	0.79	0.0006	3,183	318	251	200
	0.012	*20.00*	*0.2642*	*970.2*	*96.9*	*76.5*	*61.0*

Table B-2. High Explosive Grenades And Mines

Munition	Explosive Weight (lbs) *(kg)*	Diameter (in) *(mm)*	Maximum Fragment Weight (lbs) *(g)*	Fragment Initial Velocity (ft/s) *(m/s)*	Maximum Fragment Range		Hazardous Fragment Distance (ft) *(m)*
					Horizontal (ft) *(m)*	Vertical (ft) *(m)*	
M15 AT Mine	22.75 *10.319*	11.00 *279.40*	0.0952 *43.1727*	9,846 *3,001.1*	1,859 *566.6*	1,418 *432.2*	200 *61.0*
M21 AT Mine	10.80 *4.899*	8.87 *225.35*	0.0145 *6.5816*	10,998 *3,352.2*	1,075 *327.7*	875 *266.7*	200 *61.0*
M1A1 Anti-Tank Mine	6.00 *2.722*	7.00 *177.80*	0.0138 *6.2658*	9,891 *3014.8*	1,040 *317.0*	844 *257.3*	200 *61.0*
M16A1 AP Mine	1.13 *0.513*	3.86 *97.92*	0.0793 *35.9479*	5,585 *1,702.3*	1,492 *454.8*	1,181 *360.0*	200 *61.0*
M3 APERS Mine	0.90 *0.408*	3.50 *88.90*	0.1599 *72.5336*	3,510 *1,069.8*	1,636 *498.7*	1,250 *381.0*	201 *61.3*
M31 Rifle Grenade (Case)	0.62 *0.281*	1.29 *32.82*	0.0004 *0.1637*	11,642 *3,548.5*	351 *107.0*	290 *88.4*	200 *61.0*
M31 Rifle Grenade (Liner)	0.62 *0.281*	1.29 *32.82*	0.1610 *73.0280*	26,000 *7,924.8*	2,580 *786.4*	NA *NA*	NA *NA*
Fragmentation Grenade, M67 (approx)	0.406 *0.184*	2.52 *63.88*	0.0012 *0.5365*	7,006 *2,135.4*	464 *141.4*	377 *114.9*	200 *61.0*
MK II Grenade*	0.125 *0.057*	2.26 *57.40*	0.0142 *6.4487*	3,425 *1,043.9*	650 *198.1*	652 *198.7*	400 *121.9*
40 mm M383 (grenade)	0.12 *0.054*	1.56 *39.57*	0.0004 *0.1984*	7,707 *2,349.1*	344 *104.9*	280 *85.3*	N/C *N/C*
VB Rifle Grenade Mark I	0.11 *0.050*	1.45 *36.83*	0.0078 *3.5380*	3,660 *1,115.6*	716 *218.2*	557 *169.8*	200 *61.0*
40 mm HEDP M433 (grenade)	0.099 *0.045*	1.57 *40.00*	0.0002 *0.1048*	11,313 *3,448.2*	305 *93.0*	252 *76.8*	N/C *N/C*
40 mm M406 (grenade)	0.071 *0.032*	1.50 *38.10*	0.0004 *0.1651*	4,508 *1,374.0*	345 *105.2*	242 *73.8*	N/C *N/C*
GP Grenade M42 (submunition), (Case)	0.066 *0.030*	1.52 *38.71*	0.0004 *0.1588*	5,808 *1,770.3*	310 *94*	252 *77*	N/C *N/C*
GP Grenade M42 (submunition), (Liner)	0.066 *0.030*	1.52 *38.71*	0.0311 *0.1588*	28,000 *1,770.3*	1,710 *94*	1,311 *77*	NA *NA*

N/C Not calculated
NA Not available
*Estimated using hazard classification data

Table B-3. High Explosive Miscellaneous

Munition	Explosive Weight (lbs) *(kg)*	Diameter (in) *(mm)*	Maximum Fragment Weight (lbs) *(g)*	Fragment Initial Velocity (ft/s) *(m/s)*	Maximum Fragment Range Horizontal (ft) *(m)*	Maximum Fragment Range Vertical (ft) *(m)*	Hazardous Fragment Distance (ft) *(m)*
Bangalore torpedo M1A2	10.72	2.13	0.0026	10,810	635	520	200
	4.862	*53.98*	*1.1793*	*3,294.9*	*193.5*	*158.5*	*61.0*
Bangalore torpedo M1A2	0.86	2.13	0.0015	9,222	524	428	200
	0.390	*53.98*	*0.6804*	*2,810.9*	*159.7*	*130.5*	*61.0*
M73 Submunition	0.20	2.13	0.0020	8,059	558	454	N/C
	0.091	*54.10*	*0.9072*	*2,456.4*	*170.1*	*138.4*	*N/C*
BLU-59, BLU-26, BLU-36 Submunition	0.181	2.38	0.0015	6,278	492	396	N/C
	0.082	*60.35*	*0.6895*	*1,913.5*	*150.0*	*120.7*	*N/C*
M39 Submunition	0.052	1.44	0.0001	2,338	364	140	N/C
	0.024	*36.45*	*0.0499*	*712.6*	*110.9*	*42.7*	*N/C*

N/C Not Calculated

Table B-4. High Explosive Fuzes

Munition	Explosive Weight (lbs) *(kg)*	Diameter (in) *(mm)*	Maximum Fragment Weight (lbs) *(g)*	Fragment Initial Velocity (ft/s) *(m/s)*	Maximum Fragment Range		Hazardous Fragment Distance* (ft) *(m)*
					Horizontal (ft) *(m)*	Vertical (ft) *(m)*	
Proximity M532[A]	0.00014	0.1890	8.050E-06	8,628	104	87	104
	0.00006	*4.8006*	*0.00365*	*2,629.7*	*31.7*	*26.5*	*31.7*
Hand Grenade M206/M6	0.00264	0.2430	2.462E-05	10,638	78	66	78
	0.00120	*6.1722*	*0.01117*	*3,242.4*	*23.8*	*20.1*	*23.8*
Hand Grenade M204	0.00264	0.2430	2.462E-05	10,638	78	66	78
	0.00120	*6.1722*	*0.01117*	*3,242.4*	*23.8*	*20.1*	*23.8*
Hand Grenade M213	0.00454	0.3330	2.915E-05	11,472	83	70	83
	0.00206	*8.4582*	*0.01322*	*3,496.7*	*25.3*	*21.3*	*25.3*
Bomb Nose & Tail M907E2[A]	0.01357	1.0300	0.00153	5,347	478	385	200
	0.00616	*26.1620*	*0.69373*	*1,629.8*	*145.7*	*117.3*	*61.0*
Rocket PD M427[A]	0.01856	1.1000	0.00612	4,248	692	547	200
	0.00842	*27.9400*	*2.77766*	*1,294.7*	*210.9*	*166.7*	*61.0*
Rocket PD M423[A]	0.01856	1.1000	0.00612	4,248	692	547	200
	0.00842	*27.9400*	*2.77766*	*1,294.7*	*210.9*	*166.7*	*61.0*
Proximity M517 T178E3[A]	0.03461	1.7150	0.00866	4,997	795	633	200
	0.01570	*43.5610*	*3.92797*	*1,523.0*	*242.3*	*192.9*	*61.0*
PDD M716	0.04870	1.7020	0.00226	8,871	308	253	200
	0.02209	*43.2308*	*1.02614*	*2,703.7*	*93.9*	*77.1*	*61.0*
M557 Fuze w/ M125A1 Booster Cup	0.04900	1.7030	0.00227	8,862	308	253	200
	0.02223	*43.2562*	*1.02965*	*2,701.1*	*93.9*	*77.1*	*61.0*
MTSQ M564	0.06025	1.7040	0.00191	10,404	300	247	200
	0.02733	*43.2816*	*0.86774*	*3,171.0*	*91.4*	*75.3*	*61.0*
M-103 Nose Fuze[A]	0.12000	1.6000	0.00374	9,218	691	563	200
	0.05443	*40.6400*	*1.69643*	*2,809.6*	*210.6*	*171.6*	*61.0*
Bomb Tail MK 344 Mod 0	0.27120	1.8800	0.00390	9,896	370	304	200
	0.12301	*47.7520*	*1.77066*	*3,016.3*	*112.8*	*92.7*	*61.0*
FMU 54A/B Fuze	0.35700	2.8750	0.00645	9,031	812	657	200
	0.16193	*73.0250*	*2.92525*	*2,752.6*	*247.5*	*200.3*	*61.0*
AD Mk 395 Mod 1	0.91980	2.0020	0.00378	11,885	377	312	200
	0.41721	*50.8508*	*1.71257*	*3,622.6*	*114.9*	*95.1*	*61.0*

*Hazardous Fragment Distance set to Maximum Fragment Range when less than 200 ft

[A]These fuzes are steel rather than aluminum.

Table B-5. Chemical, Incendiary and Smoke Rounds

Munition	Explosive Weight (lbs) *(kg)*	Diameter (in) *(mm)*	Maximum Fragment Weight (lbs) *(g)*	Fragment Initial Velocity (ft/s) *(m/s)*	Maximum Fragment Range		Hazardous Fragment Distance (ft) *(m)*
					Horizontal (ft) *(m)*	Vertical (ft) *(m)*	
8 in M426 (Chemical)	7.35 *3.334*	8.00 *203.20*	3.1109 *1,411.0731*	1,365 *416.1*	2,861 *872.0*	1,893 *577.0*	421 *128.3*
115 mm M55 Rocket (Chemical)	3.20 *1.451*	4.44 *112.67*	0.1124 *50.9835*	4,386 *1,336.9*	884 *269.4*	697 *212.4*	220 *67.0*
155 mm M122 (Chemical)	2.512 *1.139*	6.10 *155.00*	1.0117 *458.8811*	1,460 *445.0*	2,167 *660.5*	1,470 *448.1*	366 *111.6*
105 mm M360 (Chemical)	1.246 *0.565*	4.13 *105.00*	0.2716 *123.2141*	1,866 *568.8*	1,647 *502.0*	1,177 *358.7*	277 *84.5*
155 mm M110 (Chemical)	0.414 *0.188*	6.10 *155.00*	0.9558 *433.5241*	612 *186.5*	1,656 *504.7*	1,178 *359.1*	261 *79.6*
105 mm M60 (Chemical)	0.349 *0.158*	4.13 *105.00*	0.2179 *98.8146*	1,058 *322.5*	1,326 *404.2*	924 *281.6*	222 *67.7*
6 lb Incendiary AN-M9X	0.281 *0.128*	2.88 *73.03*	0.0077 *3.4926*	7,659 *2,334.5*	832 *253.6*	672 *204.8*	200 *61.0*
4.2 in M2/M2A1 (Chemical)	0.143 *0.065*	4.20 *106.68*	0.0643 *29.1658*	951 *289.9*	952 *290.2*	691 *210.6*	200 *61.0*
8 in Livens (Chemical)	0.14 *0.064*	8.00 *203.20*	0.1115 *50.5966*	929 *283.2*	1,107 *337.4*	805 *245.4*	200 *61.0*
75 mm MkII (Chemical)	0.078 *0.035*	2.95 *75.00*	0.0783 *35.5197*	2,037 *620.9*	1,194 *363.9*	873 *266.1*	200 *61.0*
4.7 in. (chemical)	0.078 *0.035*	4.70 *119.38*	0.1613 *73.1641*	1,143 *348.4*	1,231 *375.2*	853 *260.0*	200 *61.0*
4 in Stokes (Chemical)	0.065 *0.029*	4.00 *101.60*	0.0499 *22.6500*	1,154 *351.7*	888 *270.7*	624 *190.2*	200 *61.0*
75 mm M1 (Chemical)	0.037 *0.017*	2.95 *75.00*	0.1004 *45.5382*	738 *224.9*	1,132 *345.0*	805 *245.4*	200 *61.0*
M15 WP Grenade	0.030 *0.014*	2.38 *60.35*	0.0034 *1.5422*	2,685 *818.4*	517 *157.6*	396 *120.7*	200 *61.0*
81 mm M375 (Chemical)	0.026 *0.012*	3.19 *81.00*	0.0248 *11.2459*	1,285 *391.7*	729 *222.2*	509 *155.1*	200 *61.0*
60 mm M302 (Chemical)	0.024 *0.011*	2.36 *60.00*	0.0253 *11.4876*	658 *200.6*	688 *209.7*	523 *159.4*	200 *61.0*
4 lb Incendiary AN-M50X-A1	0.024 *0.011*	0.96 *24.38*	0.0011 *0.5035*	3,978 *1,212.5*	406 *123.7*	323 *98.5*	200 *61.0*

Table B-6. Black Powder Rounds

Munition	Explosive Weight (lbs) *(kg)*	Diameter (in) *(mm)*	Maximum Fragment Weight (lbs) *(g)*	Fragment Initial Velocity (ft/s) *(m/s)*	Maximum Fragment Range Horizontal (ft) *(m)*	Maximum Fragment Range Vertical (ft) *(m)*	Hazardous Fragment Distance (ft) *(m)*
37 mm Mk I, LE Practice	0.034	1.4567	0.03421	1,368	816	570	200
	0.015422	*37.0000*	*15.51595*	*416.97*	*248.7*	*173.7*	*61.0*
37 mm MK II	0.527	1.4567	0.02687	1,316	1,087	847	200
	0.239042	*37.0002*	*12.18706*	*401.12*	*331.3*	*258.2*	*61.0*
60 mm TP M50	0.050	2.3622	0.02810	2,067	892	660	200
	0.02268	*59.9999*	*12.74588*	*630.02*	*271.9*	*201.2*	*61.0*
75mm MK1 (Shrapnel)	0.190	2.9528	0.02660	1,618	743	523	200
	0.086182	*75.0000*	*12.06549*	*493.17*	*226.5*	*159.4*	*61.0*
3 in Stokes	2.100	3.0000	0.00683	4,322	1,249	977	200
	0.952539	*76.2000*	*3.097566*	*1,317.35*	*380.7*	*297.8*	*61.0*
25 lb Practice Bomb MK I	2.000	3.3000	0.01875	1,300	675	472	200
	0.90718	*83.8200*	*8.503452*	*396.24*	*205.7*	*143.9*	*61.0*
155 mm Mk I Shrapnel	1.210	6.1024	0.02660	2,598	743	523	200
	0.548844	*155.0000*	*12.06549*	*791.87*	*226.5*	*159.4*	*61.0*
100 lb Practice Bomb Mk 15 Mod 3 w/ Mk 7 Spotting Signal	1.000	8.0000	0.09215	1,700	1,170	834	206
	0.45359	*203.2000*	*41.80013*	*518.16*	*356.6*	*254.2*	*62.8*

OE SECTOR

Standing Operating Procedure (SOP)

Explosive Storage and Transportation (ESAT)

PARSONS
5390 Triangle Parkway, Suite 100
Norcross, Georgia 30092

Revision No. 1
February 2005

1.0 INTRODUCTION

The purpose of this Standard Operating Procedure (SOP) is to provide the minimum procedures and safety and health requirements applicable to the acquisition, storage, accountability, and transportation of demolition material and munitions and explosives of concern (MEC).

2.0 SCOPE

This SOP applies to all site personnel involved in the acquisition, receipt, storage, handling, inventory and transportation of demolition material and MEC. It is to be followed by all Parsons and subcontractor personnel involved in any activity involving demolition material.

3.0 REFERENCES

Procedures and information contained in this document were obtained from the below-listed references:

- AR 190-11, Physical Security of Arms, ammunition and Explosives;
- AR 385-10, The Army Safety Program;
- AR 385-16, System Safety Engineering and Management;
- AR 385-64, Ammunition and Explosives Safety Standards;
- ATF P 5400.7, ATF-Explosives Law and Regulations;
- DA PAM 385-64, Ammunition and Explosives Safety Standards;
- DoD 4145.26-M, Contractors' Safety Manual for Ammunition and Explosives;
- DoD 6055.9-STD, DoD Ammunition and Explosives Safety Standards;
- EP 385-1-95a, CEHNC Basic Safety Concepts and Considerations for Ordnance and Explosives Operations;
- EM 385-1-1, USACE Safety and Health Requirements Manual; and
- EM 1110-1-4009, CEHNC Ordnance and Explosives Response

4.0 RESPONSIBILITIES

4.1 Project Manager

The Project Manager (PM), in conjunction with the Senior UXO Supervisor (SUXOS) or site manager (SM), is responsible for the initial quantity and type of demolition material ordered. This initial requisition should be of sufficient quantity to support the project for a minimum 90-day period. In the event the project is scheduled to run for less than 90 days, every effort will be made to place one requisition meeting the anticipated needs.

4.2 UXO Safety Officer

The Parsons UXO Safety Officer (UXOSO) is responsible for determining the specific site requirements for licensing, permitting, and placards. The UXOSO is also responsible to ensure the handling, storage, transport, and use of demolition material is in accordance with the approved work plan, SOPs, and federal, state and local regulations.

4.3 UXO Quality Control Specialist

The Parsons UXO Quality Control Specialist (UXOQCS) will oversee all subsequent requisitions of demolition material and will review all Purchase Order Requests (POR) for demolition material to ensure that approved Explosive Siting and Explosive Management Plans are not violated. The UXOQCS is also responsible for the inspection and auditing of the entire operation and reporting any findings to the PM. These inspections will include the acquisition procedure, documentation, storage, and transport.

4.4 Senior UXO Supervisor

The Parsons or subcontractor Senior UXO Supervisor (SUXOS) is responsible for acquiring the initial quantity and type of demolition material, submit all subsequent requests for demolition material and conduct periodic inspections of the magazine storage areas and their contents.

4.5 Vehicle driver

The vehicle driver will, at a minimum, be a UXO Tech III qualified and have a valid driver's license. This is to ensure that the driver is both experienced with and knowledgeable of demolition material. For additional transportation requirements see section 8.0.

5.0 ACQUISITION

5.1 Requisitions

Prior to ordering demolition materials, the OE Sector Purchase/Receipt Authorization List (Figure 1) must be completed and forwarded to the explosive distributor(s), along with a copy of the Parsons and/or UXO subcontractor's BATF License. Prior to the initial acquisition of explosives, Parsons must have received work plan approval from the Contracting Officer. The commercial explosives identified in Table 1 are the items approved for use. Upon approval of the WP, the initial acquisition will be processed and must be on site prior to commencing intrusive activities and all subsequent shipments must arrive in such a manner to ensure there is no break in operations.

5.2 Receipt

Only those individuals named on the Authorization list may sign for explosives from the shipper. In order to ensure that the quantity shipped is the same as the quantity listed on the shipping documents, either the SUXOS or UXOQCS, or in his absence the UXOSO, will inventory the shipment prior to signing for it.

5.3 Shipping Documents

The explosive supplier's Bill of Lading (B/L) and the freight company's shipping document generally accompany explosive shipments. The initial inventory will include reconciling the two documents with the actual shipment. Regardless of the outcome of the initial inventory, one copy of the B/L and the freight company-shipping document will be attached to a copy of the

POR and the PO. One copy of each of the four documents will be kept on file on site and one complete copy forwarded to the corporate office.

Figure 1 - Explosives Purchase / Receipt / Authorization List

Explosives Purchase / Receipt / Authorization List

Street Address and County: (Home Office)

Street or Post Office Box Address and County: (Field Office)

Federal License #: Expiration Date:

The following individuals are agents, employees, or representatives of the undersigned, and are authorized to order or acquire explosive materials on behalf of Parsons.

Name and Home Address	Driver's License No.	Soc. Sec. Number	Place of Birth

The undersigned certifies the foregoing information to be true and correct to the best of his knowledge and belief, and that he will communicate any additions or deletions to the foregoing list to Parsons.

OE Sector Operations Manager and Date (Type or print)	Signature and Date

Table 1 - DOD Hazard Classifications for Commercial Explosives

DOT EX #	NOMENCLATURE	DOD HAZARD CLASS	DATE
9806054	Cord, Detonating	1.1D	02 Dec 98
9303282	Cord Detonating, Commercial	1.1D	14 Jan 98
9207009A	Cord, Detonating	1.4D	04 Apr 00
9202035	Cord, Detonating, Commercial	1.1D	19 Sep 97
8210044	Cord, Detonating	1.1D	12 Jan 99
9709010	Cap, Blasting, Electric, Instant	1.4B - Only when in DOT packaging	27 Jan 99
9707051	Cap, Blasting, Non-electric	1.4B – Only when in DOT packaging	2 Dec 98
9303278	Cap, Non-electric, Commercial	1.1B	14 Jan 98
9104118	Cap, Blasting, Electric, Commercial	1.4B	19Sep 97
8511062	Cap, Blasting, Non-electric, Commercial	1.4B	27 Oct 97
9803207	Detonator, with Fuse Assembly	1.1B	12 Jan 99
9303277	Detonator, Cap, Electric, Commercial	1.4B	04 Apr 00
8912113	Demo Charge, C-4, Commercial	1.1D	27 Jan 99
9608031	Booster, 1 LB	1.1D	14 Jan 98
9308432	Booster, Pentolite	1.1D	14 Jan 98
8611125	Booster, Pentex	1.1D	14 Jan 98
9303285	Booster, Cast. Austin	1.1D	14 Jan 98
9508033	Fuse Lighter, Commercial	1.4S	27 Oct 97
9201092	Fuse, Time, safety	1.4S	2 Dec 98
8311105	Fuse, Safety, Commercial	1.4S	27 Oct 97
9404156	Shock Tube, Shock Star MS	1.4S	14 Jan 98
9106259	Shock Tube, Excel MS	1.4S	14 Jan 98
9608028	Shaped Charge, Commercial	1.4D	19 Sep 97
9405290	Shaped Charge, Commercial	1.4D	10 Mar 99
9409002	Shaped Charge, commercial	1.4D	27 Oct 97
8601111	Shaped Charge, Commercial	1.4S	10 Mar 99

Note: CEHNC-OE-S-P maintains supporting documentation.

5.4 Receipt Discrepancies

Upon receipt, the type, quantity, and lot number of each item will be checked against the manifest and entered on the Magazine Data Card(s) (Figure 2). In the event there is a discrepancy between the amount shipped and the amount received, the SUXOS or the UXOQCS will immediately contact the explosive supplier and inform him of the discrepancy. It then is the responsibility of the supplier and shipper to rectify the situation and inform Parsons of the

results. The supplier and/or shipper must then correct their documents and forward them to the site. In any event, only the amount received will be entered on the Magazine Data Card(s), which will be kept in the magazine and annotated for each transaction.

5.5 Reporting Lost or Stolen Explosives

5.5.1 Loss or theft of explosives will be reported as required in 27 CFR Part 55, Sub part C paragraph 55.30. ATF Form 5400.5 will be completed, within 24 hours and forwarded to the ATF, with a copy to the contracting officer. A copy of this form is provided in Figure 5.

5.5.2 The following individuals will be notified immediately upon discovery of theft of explosive:

- Site Manager, Project Manager and USACE Safety Representative
- USACE Project Manger and Contracting Officer
- Bureau of Alcohol, Tobacco and Firearms (ATF) at 1-800-800-3855
- Project subcontracted UXO firm or supplier of explosives

6.0 STORAGE AND SECURITY

Approved explosive storage facilities may be provided at the site, either by the U.S. Army Corps of Engineers (USACE) or by the installation. Parsons will use the existing magazines for explosive storage and comply with local storage criteria and procedures. The SUXOS and/or UXOQCS will prepare Magazine Data Card(s) (Figure 2). If no explosives storage facilities are available, Parsons will:

- Use approved BATF Type 2 structures;
- Locate, install, and maintain the magazines to comply with the magazine criteria and quantity distance requirements established in *DOD 6055.9-STD, DOD Ammunition and Explosives Safety Standards;*
- Install sufficient magazines to comply with the explosive compatibility requirements, (i.e., bulk explosives, initiating explosives);
- Establish security, such as fencing, to prevent unauthorized access and/or theft, as required.

Figure 2 - Magazine Data Card

				MAGAZINE DATA CARD				
Product Code / FSN:		Nomenclature:			Site Name: Address:			
Date Code / Lot Number		Hazard Class	UN or NA	Quantity / Case:				
Date	Bill of Lading /Voucher Number	Received From	Quantity Received	Quantity Issued	Issued To	Current Balance	Initials	
							Issuer	Receiver

6.1 Exterior Construction

BATF Type 2 magazines are required to have the exterior and doors to be constructed of not less than 3/16-inch steel and lined with at least two inches of hardwood. Magazines with top openings will have lids with water-resistant seals, or which overlap the sides by at least one inch when in a closed position.

6.2 Hinges and Hasps

Hinges and hasps will be attached to doors by welding, riveting, or bolting with the nuts on inside of door. Hinges and hasps will be installed so they cannot be removed when the doors are closed and locked.

6.3 Locks

Each door will be equipped with two padlocks fastened in separate hasps and staples. Padlocks must have at least five tumblers or five blades, and a casehardened shackle of at least 3/8-inch diameter. Padlocks will be protected with not less than 1/4-inch steel hoods constructed so as to prevent sawing or lever action on the locks, hasps, and staples.

6.4 Signage/Placards

ATF and DoD require that all magazines be appropriately posted for content hazard class, fire fighting hazard, and an emergency notification list. Magazines will be placarded in accordance with *DoD 4145.26M and DA Pam 385-64.* In most instances, this will require a Fire Division Class 1 for the recovered UXO storage magazines and a Fire Division Class 3 for the demolition material, excluding detonators, which are Fire Division Class 4. If in doubt label the contents with the next highest hazard. In the event there are two different fire division or hazard class items in the same magazine, use the higher hazard division/class placard.

6.5 Lightning Protection

Appropriate lightning protection will be installed on all site(s), IAW *DA Pam 385-64, Chapter 6, paragraph 6-13; Table 6-1 and 6-2 and Chapter 12, paragraphs 12-5, 12-8:*

- A qualified person will conduct a resistivity test, over several points of the proposed site. Test boring will be used for deciding on an adequate earth electrode system. The minimum resistance is 25 ohms measured on a Ground Resistance Tester (*Biddle Ground Megger®).*
- An Earth Electrode Subsystem will be placed at uniform intervals around the protected facility as required; grouping of earth electrodes on one side of a facility is prohibited. Earth electrodes will be set not less than 3 feet or more than 8 feet from the structure(s).
- Grounding Rods will not be less than ¾" in diameter and 10 feet in length. Rods will be copper-clad steel, solid copper or stainless steel and free of paint or other non-conductive coating. The minimum number of rods for the facility is two, yet may be increased to assist in the reduction of resistivity. Rods will be located clear of paved surfaces, walkways and roadways and will be driven into the ground so that the tops are at least 12" below finished grade. In the event of shallow topsoil over bedrock or dense coral preventing the burial of rods, use extended down conductors or buried open plates, as described in *Chapter 3 of National Fire Protection Association 780.*
- Bonding is used to reduce the possibility of a side flash and to ensure lightning current produces no electrical potential differences. For a building 36 feet in height or less, a bonding strap is required for large masses of metal (400 in sq) located on the exterior (door), or within the facility.

- Lightning warning systems provide a positive, reliable means of continuously monitoring and recording atmospheric voltage gradient. For those sites without a lightning warning system, the UXOSO will establish criteria for terminating ammunition and explosive operations and evacuate the facility to the MSD distance, as outlined in the Work Plan.
- Periodical inspections and test requirements for the grounding system will be accomplished every 6 months for visual inspections and every 24 months for electrical tests. The grounding system will have a resistance of 25 ohms or less and the bonding strap 1 ohm or less. The results of these tests will be kept on file at the site.

Sites that do not need a Lightning Protection System (LPS) must meet the following requirements, in accordance with *EM 1110-1-4009, Chapter 11*.

- The magazine is constructed of metal that is 3/16-inch steel or larger.
- The magazine is grounded as described in Figure 3.
- The magazine is located at least 7.0 feet from the nearest fence. Figure 3 is an example of a typical site not requiring an LPS.

6.6 Fencing Protection

Appropriate fencing (physical security) protection will be installed on all site(s), in accordance with *AR 190-11, paragraph 5-3:*

- Fence Fabric will be of chain link (galvanized, aluminized or plastic coated woven steel) 2-inch square mesh 9-gauge diameter wire, including coating.
- Posts, bracing and other structure members will be located on the inside of the fence fabric. Galvanized steel or aluminized wire-ties equal in gauge to fencing will be used to secure the fence fabric to the posts or other structural members.
- The minimum height of the fence fabric will be 6 feet without an outrigger.
- The bottom of the fence fabric will extend to within 2 inches of firm ground. A 9-gauge retaining wire, of the same material as the fence, will be interwoven along the bottom portion of the fence from post to post, in order to prevent anyone from pushing the fence in at the bottom. Surfaces will be stabilized in areas where loose sand, shifting soils, or surface waters may cause erosion and thereby assist an intruder in penetrating the fenced area. Where surface stability is not possible or is impracticable, concrete curbs, sills or other suitable type anchoring devices, extending below ground level will be provided.
- The barrier will have a minimum number of vehicular and pedestrian gates, consistent with the operational requirements. These gates will be structurally comparable to the adjacent fence. Gates will be provided with an approved lock and hinge pins and hardware will be welded or otherwise modified to prevent easy removal.

6.7 Emergency Notification List

An emergency notification list containing the names, telephone numbers, and local addresses of the individuals to be notified in the event of an emergency, will be posted on the outside and inside of the magazine door. These individuals should be the same individuals authorized to sign for explosives, as well as the site manager and UXOSO if they are not on the authorized signature list.

6.8 Compatibility

Explosive compatibility will be maintained in accordance with *DA PAM 385-64 and TM9-1300-206.* Table 2 lists the various storage compatibility groups and Table 3 is the storage compatibility chart. In certain instances, it may be necessary to store incompatible items in the same magazine. If this should occur, a waiver will be requested IAW DOD 6055.9-STD., and then a barricade, such as sandbags, within the magazine, will physically separate the incompatible items.

6.9 Key Control

Magazines will remain locked except when receipts and issues are being made. The two locks on the magazines will require two different keys to unlock. The SUXOS will keep one key and the second key will be kept by the UXOQCS, or in his absence, the UXOSO. This procedure ensures that no one individual can gain access to the magazines.

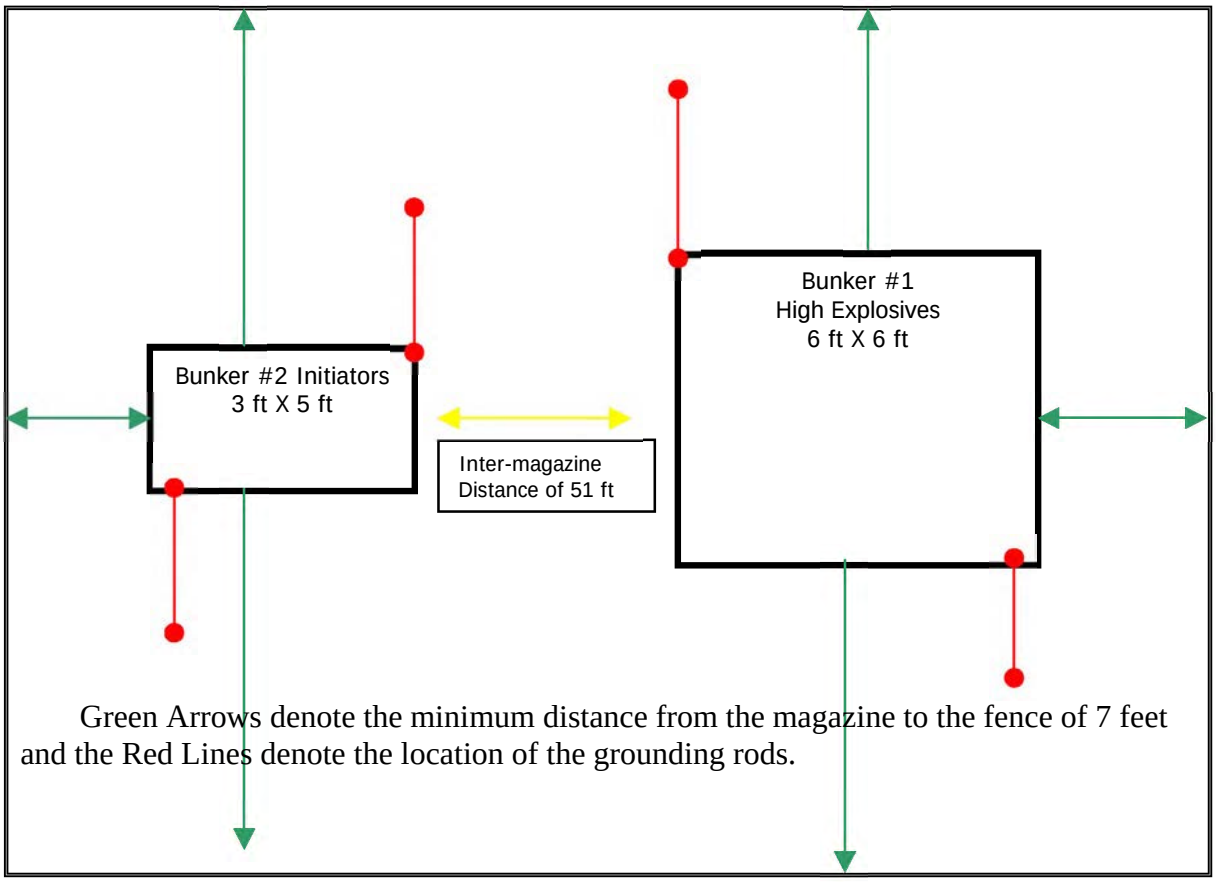
6.10 Inspection

At the start of each workday, a physical check will be made of the magazine storage area to ensure security has not been compromised.

6.11 Security

Physical security of the explosive storage location, if on a military installation, is provided by the installation. Parsons provides security of the explosive storage location on civilian property, which consists of the required fencing and daily inspections excluding non-work days unless the magazine is considered to be vulnerable to being vandalized.

Figure 3 - Typical Layout of a Non-LPS Storage Site



Notes: Based on *Table C9.T5, DOD 6055.9STD a* minimum of 51 feet for inter-magazine distance (100 lbs NEW) is required (yellow arrow). The fenced area is 1,520 square feet, based on 76ft in length and 20ft wide. It is recommended that a single magazine, equipped with an attached detonator outrigger be used whenever possible in order to decrease the size of the fenced area required.

Table 2 - Storage Compatibility Groups

STORAGE COMPATIBILITY GROUPS FOR EXPLOSIVES AND AMMUNITION	
GROUP A	
Cyclonite (RDX), dry	Mercury fulminate, wet
HMX, dry	PETN, dry
Lead azide, wet	RDX (cyclonite), dry
Lead styphnate, wet	Tetracene, wet
GROUP B	
Fuses (except chemically-actuated fuses containing ampules which may initiate, directly or indirectly, explosives and explosives-loaded components which are assembled in the conventional manner to form the finished explosive fuse).	Detonators
	Mines, practice, AP, M17
	Percussion elements
	Primer detonators
GROUP C	
Ammunition, blank and saluting, cannon	Cartridge, 90mm, canister, AP
Ammunition, .50 caliber, except API/incendiary	Cartridges, practice, over 40mm
Ammunition, 20mm, practice and high pressure test	Catapults, aircraft ejection seat, M3A1, M4A1, M5
Ammunition, 25mm, with inert projectile	Charge, propelling, not assembled to projectiles EC powder
Ammunition, 27mm, caseless	Detonating cord (primacord)
Ammunition, 30mm, ball and high pressure test	Nitrocellulose
Ammunition, 30mm, practice and training	Fuel (solid), emergency power unit
Ammunition, 37mm and 40mm, TP and AP	Propellant
Ammunition, 40mm, practice, M407A1, M382, and M385	Rockets, practice, 3.5-inch
Benite	Rocket motors, M3, M5, M6, M10, M13, M26, M30, M37, M42, M53, M66; Pershing 1st and 2nd stages; Spartan 1st, 2nd, and 3rd stages
Baron potassium nitrate	
GROUP D	
Adapter booster	Explosive D
Ammonium nitrate, except in original shipping container or equivalent	Explosives, cratering
Ammonium perchlorate, except when particle size is over 15 microns and in original shipping container or equivalent	Grenades, rifle, AT (except pentolite loaded)
Ammonium picrate (Explosive D)	HMX, wet
Bangalore torpedoes	Mine, APERS, MN, M14 (w/integral fuse)
Baratol	Mines, antipersonnel (bounding type
Black powder, bulk	Mines, antipersonnel (cast iron block)

Table 2 – Storage Compatibility Groups (Cont'd)

Bombs, demolition	Mines, HEAT Nitrocellulose wet 8-30% water exposed to detonation hazards at less than intra line distance
Bombs, fragmentation	Nitroguanidine
Bombs, general purpose	Nitrostarch Octol
Boosters	PBX
Boosters, auxiliary	pentolite
Bursters	PETN, wet
Charge, demolition, snake	Picratol
Charge, springing earth rod, blast driven	Picric acid
Charge, supplementary, HE	Projectiles, HE, fuzed or unfused
Compositions A, A-2, A-3, A-4, B, B-3, C, C-2, C-3, and C-4	RDX (Cyclonite), wet
Cutter, cable M1	Rocket heads, HE and HEAT (except pentolite loaded) w/o motors
Cyclonite (RDX), wet	Shaped charges
Cyclotol	Tetranitrocarbazole (TNC)
Demolition Blocks	Tetryl
Destructor, HE, M10	Tetrytol
Detonating cord (primacord) exposed to detonation hazard at less than intra line distance	TNT
Dynamite	Tritonal
Ednatol	Torpex

Table 2 – Storage Compatibility Groups (Cont'd)

GROUP E	
Ammunition, HEP	Ammunition, fixed and semifixed, 90mm through 106mm, loaded with ammonal, amatol, Explosive D, composition B or TNT
Ammunition, 20mm, HE, HEI and functional packs containing HE and HEI	Cartridge, heavy mortar, over 81mm (including 81mm M56), except chemical loaded
Ammunition, 30mm, HEDP	Cartridge, light mortar, 81mm or less (excluding 81mm M56), except chemical loaded
Ammunition, 37mm, HE	Redeye guided missiles, packaged 3 complete rounds w/launcher
Ammunition, 40mm, HE, RDX loaded	
Ammunition, 40mm, HE, M406, M386, M441, and M463	Rockets, HEAT, 3.5-inch, complete round
Ammunition, 57mm through 81mm, except WP smoke, HEP and blank	Rockets, HE, 2.75-inch (in LAU-3/A rocket launcher)
GROUP F	
Grenades, hand offensive	Grenades, fragmentation
GROUP G	
Ammunition, .50 caliber API and incendiary	Grenades, hand, CN1, ABC, M25A1, w/fuse C12
Ammunition, 20mm, API	Grenades, hand, CM1, ABC, M25A2, w/fuse C12
Ammunition, 20mm, incendiary and functional packs containing incendiary, except those containing HE or HEI	Grenades, illuminating and incendiary
Ammunition, 40mm, riot control and pyrotechnic loaded, except WP smoke	Grenades, practice, w/spotting charge
Bombs, photoflash	Grenades, rifle, smoke, XM48E1 and M22 and M23
Cartridge, igniter, M2	Grenades, smoke (except WP and PWP)
Cartridge, illuminating	Grenades, riot control, CS1, M25A2
Cartridge, photoflash	Igniter, spotting charge
Cartridge cases, primer (w/o propellant)	Igniters for rocket motors (e.g., M12, M18, M20 and M29)
Charge, igniter assembly, for practice hand grenades	Ignition cartridge for trench mortar ammunition
Charge, spotting, APR practice, M8	Illuminating compositions (consolidated in final press operations)
Chemical ammunition, Group B, tear or smoke producing, w/explosive components, over 40mm	Mines, practice, w/spotting charge and/or fuse
Chemical ammunition, Group B, tear or smoke producing, w/o explosive components	Nuclear fire marker device 11-F2

Table 2 – Storage Compatibility Groups (Cont'd)

Chemical ammunition, Group D, containing flammable solids, except for TEA or TPA, w/o explosive components	Photoflash powder
Chemical ammunition, Group D, fixed or semi-fixed rounds, containing flammable solids, except for TEA or TPA	Primers, artillery and cannon, percussion and electric
Clusters, incendiary bomb, M31 and M32 (w/o fuzing components)	Projectiles, illuminating
Destroyer, file, M4	Rocket, riot control agent, CS, 2.75-inch FFAR, MX99
Detonation, simulator, explosive M80	Simulators, M110, M115, M116, M117, M118, M119 and XM142
Grenade, hand, smoke, HC, M8	Smoke pots
Grenades, hand, CN, M7A1, w/fuse M201A1	Spotting charges (cartridge for miniature practice bombs)
Grenades, hand, CS, M7A3, w/fuse M210A1	
GROUP H	
Chemical ammunition, Group C	Grenade rifle, WP, M19
Grenades, WP	
GROUP J	
Chemical ammunition, Group D, containing flammable liquids or gels, with or w/o explosive components	Chemical ammunition, Group D, fixed and semifixed rounds, containing flammable liquids or gels with or without explosive components
GROUP K	
Chemical ammunition, Group A, with or without explosive components	Chemical ammunition, Group B, with or without explosive components, designed for toxic or incapacitating effects greater than lachrymation
Rockets, toxic chemical agents, complete rounds	

Table 2 – Storage Compatibility Groups (Cont'd)

GROUP L	
Aluminum powder	Fuzes, chemically-actuated, containing ampoules which may initiate directly or indirectly, explosives and explosives loaded components which are assembled in the conventional manner to form the finished explosive fuse
Ammonium nitrate	Magnesium powder
Ammonium perchlorate	Grenades, rifle, AT (pentolite loaded)
Ammunition, pentolite loaded	Nitrates (inorganic), except ammonium nitrate (in original shipping container or equivalent)
Chemical Ammunition, Group A, without explosive components	Perchlorates
Chemical ammunition, Group B, without explosive components, designed for toxic or incapacitating effects more severe than lachrymation	Peroxides, solid
Chemical ammunition, Group D, TEA or TPA components	Rocket heads, pentolite loaded, w/o motors
Chlorates	Zirconium (types I and II, spec. FED 1665)
DNT	
GROUP S	
Ammunition, 40mm, canister and multiple projectile	Fuse lighters
Ammunition, small arms, less than .50 caliber	Fuse safety
Explosive bellows	Squibs commercial
Firing devices	

Table 3 - Storage Compatibility Chart

Groups	A	B	C	D	E	F	G	H	J	K	L	N	S
A	**X**	**Z**											
B	**Z**	**X**	**Z**	**Z**	**Z**	**Z**	**Z**					**X**	**X**
C		**Z**	**X**	**X**	**X**	**Z**	**Z**					**X**	**X**
D		**Z**	**X**	**X**	**X**	**Z**	**Z**					**X**	**X**
E		**Z**	**X**	**X**	**X**	**Z**	**Z**					**X**	**X**
F		**Z**	**Z**	**Z**	**Z**	**X**	**Z**					**Z**	**X**
G		**Z**	**Z**	**Z**	**Z**	**Z**	**X**					**Z**	**X**
H								**X**					**X**
J									**X**				**X**
K										**Z**			
L													
N		**X**	**X**	**X**	**X**	**Z**	**Z**					**X**	**X**
S		**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**			**X**	**X**

Notes:

1. The marking “X” at the intersection of the above chart indicates that these groups may be combined in storage. Otherwise, mixing is either prohibited or restricted per Note 2 below.
2. The marking “Z” at an intersection of the above chart indicates that, when warranted by operational considerations or magazine non-availability, and when safety is not sacrificed, these groups may be combined in storage.
3. The marking “U” on the above chart indicates that leaking toxic chemical munitions of one agent type, i.e., GB, with or without explosive components, may be stored together in one magazine specifically designated for storage of leakers of that agent type.
4. Equal numbers of separately packaged components of complete rounds of any single type of ammunition may be stored together. When so stored, compatibility is that of the assembled rounds; i.e., WP Filler in Group H, HE Filler in Groups D, E, or F, as appropriate.
5. Group K required not only separate storage from other groups, but also requires that munitions having different toxic chemical agent fillers be stored separately from each other.
6. Ammunition designated “PRACTICE” by NSN and nomenclature may be stored with the fully loaded ammunition it simulates.

7.0 INVENTORY

Upon receipt and verification of explosive demolition material, the Magazine Data Card(s) is/are filled out and kept in the magazine on top of the listed item. A duplicate copy is maintained by the UXOQCS or SUXOS and kept on file in the site office.

7.1 Usage Inventory

Following each occurrence of a receipt or issue of explosive material, the UXOQCS will conduct a joint inventory in conjunction with the demo team leader, drawing out or returning the explosives. Only those items issued/returned will be inventoried and the two sets of Magazine Data Cards will be appropriately annotated.

7.2 Monthly Inventory

The last work day of each month, the UXOQCS, and SUXOS or the USACE Safety Specialist and UXOSO will conduct an inventory and record results on the two sets of Magazine Data Cards.

7.3 Discrepancies

In the event there is a discrepancy during any inventory, the item will be recounted a minimum of two additional times. If a discrepancy still exists, the USACE PM, Contracting Officer, and BATF will be telephonically notified with a written report submitted within 24 hours of the discovery.

7.4 Procedures for Return to Storage of Explosives not Expended

Explosives that were issued for use but were not needed will be returned daily to the magazines at the completion of disposal operations. The Demolition Team Leader will return the unused explosives to the storage magazine and revise the Magazine Data Card(s) and Explosives Use Record (Figure 4).

7.5 Disposal of Remaining Explosives

Parsons is required by BATF to account for all explosives purchased and used. At project completion, the UXOQCS and PM will conduct an economic analysis of the disposition alternatives for the unused explosives. A written request to the CEHNC Contracting Officer will be made listing the alternatives and requesting disposition of the unused explosives. Based on that decision, the unused explosives will be transferred or disposed of as directed. For Firm Fixed Priced (FFP) contracts this is not required. The unused explosives will be disposed of as determined by the PM and UXOQCS.

Figure 4 – Explosives Usage Record

Explosive Usage Record

Team Number: Date: Project Name:

Team Leader: Work Areas & Grid Numbers:

Explosives Issued Signature of Team Leader:

Item	Quantity	Lot Number	Checkers Initials

Explosives Expended Signature of Team Leader

Item	Quantity	Lot Number	Checkers Initials

Explosives Returned Signature of SUXOS:

Item	Quantity	Lot Number	Checkers Initials

The signatures in each section of this document indicate that the items listed in that section were in fact issued, expended, or returned to storage and that the quantities listed were verified through a physical count.

8.0 Transportation

Transportation of MEC will comply with all Federal, state, and local regulations. Permits are not required under CERCLA for on-site or on Federal installation transportation of

demolition material or MEC. Off-site transportation of demolition material or MEC will not be accomplished until coordination and approval has been received from the USACE Contracting Officer. Off-site shipment of demolition material or MEC will be made using commercial carriers approved to transport ammunition and explosives. For off-site shipment:

- MEC will be packaged in accordance with *49 CFR parts 172 and 173*, if possible; if not possible the MEC will be transported in such a manner as to not move or touch other MEC items.
- Drivers will be provided with Emergency Response Information, Figure 6;
- Vehicles will be inspected using the Motor Vehicle Inspection Form (Figure 7), and, if applicable, be properly placarded;
- Compatibility requirements will be observed;
- The load shall be well braced and, except when placed in an enclosed vehicle, covered with a fire-resistant tarpaulin.

8.1 General Highway Transport

In most instances, the following data presented is sufficient to meet the requirements for explosive transport.

8.2 Commercial Motor Vehicle Requirements *(49CFR Part 383.5)*

Commercial motor vehicle (CMV) means a motor vehicle, or a combination of motor vehicles, used in commerce to transport passengers or property if the motor vehicle

- Has a gross combination weight rating of 11,794 or more kilograms (26,001 pounds or more), inclusive with a towed unit with a gross vehicle weight rating of more than 4,536 kilograms (10,000 pounds); or
- Has a gross vehicle weight rating of 11,794 or more kilograms (266,001 pounds or more); or
  - Is designed to transport 16 or more passengers, including the driver; or
  - Is of any size and is used in the transportation of materials found to be hazardous for the purposes of the Hazardous Materials Transportation Act, and which require the motor vehicle to be placarded under the *Hazardous Materials Regulations (49 CFR part 172, subpart E).*

FIGURE 5
ATF FORM 5400.5, REPORT OF THEFT OR LOSS-EXPLOSIVE MATERIALS

Form Approved, OMB No. 1512-0065 (04/30/96)

DEPARTMENT OF THE TREASURY
BUREAU OF ALCOHOL, TOBACCO AND FIREARMS
REPORT OF THEFT OR LOSS-EXPLOSIVE MATERIALS

DATE

Upon discovery of any theft or loss of any of your explosive materials:
-First, call ATF toll free at 1-800-800-3855 (or call ATF collect at 1-800-800-3855 if you are in Alaska, Guam, Hawaii, Puerto Rico or the Virgin Islands) to report the theft or loss;
-Second, call your local law enforcement office to report the theft or loss; and
-Third, complete this form and attach any additional sheets or invoices necessary to provide the required information, and mail to the nearest ATF office listed on the reverse. We suggest you retain a copy of the completed form. Please complete each item as applicable, to the best of your ability.
NOTE: Section 842(k), 18 U.S.C. Chapter 40, states, "It shall be unlawful for any person who has knowledge of the theft or loss of any explosive materials from his stock to fail to report such theft or loss within twenty-four hours of discovery to the Secretary and to appropriate local authorities." Codified at 27 C.F.R. Section 55.30.

1. NAME, ADDRESS AND TELEPHONE NUMBER OF PERSON MAKING REPORT (include corporate or business name, if applicable)

2. Location of theft or loss (if different from item 1)

3. THEFT OR LOSS	DATE	TIME
a. DISCOVERED		
b. OCCURRED (Show approximate if exact is not known)		
c. REPORTED TO ATF BY TELEPHONE		
d. REPORTED TO LOCAL AUTHORITIES		

4. NAME AND ADDRESS OF LOCAL AUTHORITY TO WHOM REPORTED

5. EXPLOSIVE MATERIALS LOST OR STOLEN (Attach invoices or additional sheets, if necessary)

a. MANUFACTURER OR BRAND NAME (Include date and shift code)	b. QUANTITY (Pounds of Explosives, Number of Caps)	C. TYPE AND DESCRIPTION (Dynamite, Blasting Agents, Detonators, etc. Include for each type, size, MS delay or length of leg wire, as applicable)

6. THEFT OR LOSS OCCURRED FROM (Check applicable box)
☐ PERMANENT MAGAZINE ☐ PORTABLE MAGAZINE ☐ TRUCK ☐ WORK SITE ☐ OTHER (Explain)

7. ENTRY TO MAGAZINE MADE THROUGH (Complete if applicable)
☐ DOOR ☐ ROOF ☐ FLOOR ☐ FOUNDATION
☐ WALL ☐ CEILING ☐ VENTS ☐ OTHER (Explain)

8. NUMBER AND TYPE OF LOCKS FORCED (Complete if applicable)

9. OTHER INFORMATION PERTINENT TO THE THEFT OR LOSS

10. SIGNATURE AND TITLE OF PERSON MAKING REPORT

11. FEDERAL EXPLOSIVE LICENSE OR PERMIT IF ANY

FOR ATF USE ONLY

DATE RECEIVED	TIME RECEIVED	UNIQUE IDENTIFIER

ATF F 5400.5 (1-93) PREVIOUS EDITIONS ARE OBSOLETE

Figure 6 – Emergency Response Information

SHIPPING PAPER AND EMERGENCY RESPONSE INFORMATION FOR HAZARDOUS MATERIALS					
THIS VEHICLE IS TRANSPORTING HAZARDOUS MATERIALS					
Date Prepared:	Date of Travel:			Page_____of_____	
Proper Shipping Name	**Hazard**	**ID No.**	**PG**	**Qty/Units**	**Weight**
Emergency notification. In all cases of accident, incident, breakdown or fire, prompt notification must be given. **FOR EMERGENCY RESPONSE INFORMATION, SEE BACK OF THIS FORM**					
Remarks:					
Certification: This is to certify that the above named materials are properly classified, described, packaged, marked, and labeled, and are in proper condition for transportation according to the applicable regulations of the Department of Transportation.					
Signature of Shipper Representative:	Signature of Vehicle Operator(s):				
24-Hour Emergency Assistance Telephone Numbers:	Work Hours Emergency Phone Numbers:				

Figure 6 – Emergency Response Information (Cont'd)

EMERGENCY RESPONSE INFORMATION

Guide Number 46 and 50 from the U.S. Department of Transportation Emergency Response Guide Book P 5800.6 are reproduced hereon. These guides are applicable to Hazard Class 1 Materials (Explosives).
Mark an X in the appropriate box:

☐ **USE GUIDE 46 FOR EXPLOSIVES (1.1), (1.2), (1.3), (1.5), AND (1.6)**

☐ **USE GUIDE 50 FOR EXPLOSIVES (1.4)**

For all other hazardous materials or substances, annotate appropriate Emergency Response Guide Book Guide Number in the block below, and attach a copy of the guide number page or pages.

Guide Numbers:

GUIDE 46 (ERG 93)

POTENTIAL HAZARDS

FIRE OR EXPLOSION:

May explode and throw fragments 1 mile or more if fire reaches cargo.

HEALTH HAZARDS:

Fire May produce irritating or poisonous gases.

EMERGENCY ACTION

If fire reaches cargo, do not fight fire.

If you know or suspect that heavily-encased explosives, such as bombs or artillery projectiles are involved, stop all traffic and begin to evacuate all persons, including emergency responders, from the area in all directions for 5000 feet (1 mile) for rail car or 4000 feet (3/4 mile) for tractor/trailer.

When heavily-encased explosives are not involved, evacuate the area for 2500 feet (½ mile) in all directions.

Positive pressure self-contained breathing apparatus (SCBA) and structural firefighters' protective clothing will provide limited protection.

CALL Emergency Response Telephone Number on Shipping paper FIRST. If Shipping Paper NOT AVAILABLE or NO ANSWER, CALL CHEMTREC AT 1-800-424-9300.

FIRE

Cargo Fires: DO NOT FIGHT FIRE WHEN IT REACHES CARGO. Withdraw from area and let fire burn.

Truck and Equipment Fires: Try to prevent fire from reaching the explosive cargo compartment. Flood with water; if no water is available use Halon, dry chemical or earth.

Promptly isolate the scene by removing ALL PERSONS from the vicinity of the incident if there is a fire. First, move people out of line-of-sight of the scene and away from windows. Then, obtain more information and specific guidance from competent authorities listed on the shipping papers.

SPILL OR LEAK

Shut off ignition sources; no flares, smoking or flames in hazard area. Do not touch or walk through spilled material.

FIRST AID

Call emergency medical care.
Use first aid treatment according to the nature of the injury.

GUIDE 50 (ERG 93)

POTENTIAL HAZARDS

FIRE OR EXPLOSION:

May explode and throw fragments 1/3 mile or more if fire reaches cargo.

HEALTH HAZARDS:

Fire May produce irritating or poisonous gases.

EMERGENCY ACTION

If fire reaches cargo, do not fight fire.

Stop all traffic and begin to evacuate all persons, including emergency responders, from the area for 1500 feet (1/3 mile) in all directions.

Positive pressure self-contained breathing apparatus (SCBA) and structural firefighters' protective clothing will provide limited protection.

CALL Emergency Response Telephone Number on Shipping paper FIRST. If Shipping Paper NOT AVAILABLE or NO ANSWER, CALL CHEMTREC AT 1-800-424-9300.

FIRE

Cargo Fires: DO NOT FIGHT FIRE WHEN IT REACHES CARGO. Withdraw from area and let fire burn.

Truck and Equipment Fires: Try to prevent fire from reaching the explosive cargo compartment. Flood with water; if no water is available use Halon, dry chemical or earth.

Promptly isolate the scene by removing ALL PERSONS from the vicinity of the incident if there is a fire. First, move people out of line-of-sight of the scene and away from windows. Then, obtain more information and specific guidance from competent authorities listed on the shipping papers.

SPILL OR LEAK

Shut off ignition sources; no flares, smoking or flames in hazard area. Do not touch or walk through spilled material.

FIRST AID

Call emergency medical care.
Use first aid treatment according to the nature of the injury.

SUPPLEMENTAL INFORMATION

Packages bearing the 1.4S label contain explosive substances or articles that are designed or packaged in such a manner that when involved in a fire, may burn vigorously with localized detonations and projection of fragments; effects are usually confined to immediate vicinity of packages.

If fire threatens cargo area containing packages bearing the 1.4S label, consider initial isolation of at least 50 feet in all directions. Fight fire with normal precaution from a reasonable distance.

8.3 CDL Requirements

As long as site personnel are not using vehicles that weigh more than 26,000 pounds and are not transporting any materials that must be placarded under the DOT Hazardous Materials Regulations (i.e., they are only transporting 1.4 explosives), then the vehicle being used need not be classified as a CMV and the operator of the vehicle need not have a Commercial Driver's License (CDL). This is the typical situation for site personnel since they usually transport relatively small quantities of 1.4 demolition materials. However, if a CDL is required, the PM or UXOSO will ensure that the requisite license/permits are obtained.

8.4 Federal Installations/On-Site

Transportation of demolition material and MEC on-site and on Federal installations will comply with the following:

- Vehicles will be inspected per occurrence and will be properly placarded;
- Explosives will be transported in closed vehicles whenever possible. When using an open vehicle, explosives will be covered with a flame resistant tarpaulin (except when loading/unloading);
- Vehicle engine will not be running. Wheel chocks and brakes set when loading/unloading explosives;
- Beds of vehicles will have either a plastic bed liner, dunnage, or sandbags to protect the explosives from contact with the metal bed and fittings;
- Vehicles transporting explosives will have a first aid kit, two 10 ABC rated fire extinguishers, and communications capabilities;
- Initiating explosives, such as detonators, will remain separated from other high explosives during loading, unloading, and while on vehicles;
- Compatibility requirements will be observed;
- Operators transporting explosives will have a valid drivers license; and
- Drivers will comply with posted speed limits, but will not exceed a safe and reasonable speed for conditions. Vehicles transporting explosives off-road will not exceed 25 mph.

8.5 Off-Site Transportation of Explosives over Public Highway

8.5.1 DOT Certificate of Registration

As long as only 1.4 explosives or less than 55 net explosive weight (NEW) of 1.1, 1.2, or 1.3 explosives are transported by personnel, DOT certificates of registration for individuals involved in the transportation of demolition materials are not required.

8.5.2 Mixed Packaging Requirements

Explosives of compatibility Group S may be packed with explosives of all other explosive compatibility groups except A and L. To determine the compatibility of the materials typically transported by site personnel, check the Material Data Sheets presented in Attachment 1.

8.6 General Placard Requirements

Those munitions response sites that require placards will accomplish this IAW 49 CFR 172.504. The placard requirements listed below will apply to explosives transportation, if applicable:

> "(a) Except as otherwise provided, each bulk packaging, freight container, unit load device, transport vehicle or rail car containing any quantity of a hazardous material must be placarded on each side and each end with the type of placards specified in Tables 4 and 5, in accordance with other requirements and exceptions."
>
> "(c) Exceptions for less than 454 kg (1,001 pounds). Except for bulk packaging and hazardous materials subject to § 172.505, when hazardous materials covered by Table 5 of this section are transported by highway or rail, placards are not required on:
>
> (1) A transport vehicle or freight container which contains less than 454 kg (1,001 lbs.) aggregate gross weight of hazardous materials covered by Table 5 of paragraph (e) of this section; or
>
> (2) A rail car loaded with transport vehicles or freight containers, none of which is required to be placarded."

The exceptions provided in paragraph (c) provided above do not prohibit the display of placards in the manner prescribed in this subpart, if not otherwise prohibited (see § 172.502), on transport vehicles for freight containers, which are not required to be placarded.

Table 4: General Placard Requirements

Category of material (Hazard class or division number and additional description, as appropriate)	Placard name	Placard Design Section Ref. (§)
1.1	Explosives 1.1	172.523
1.2	Explosives 1.2	172.524
1.3	Explosives 1.3	172.525
2.3	Poison Gas	172.532
4.3	Dangerous When Wet	172.528
6.1 PG I, inhalation hazard only)	Poison	172.542
7 (Radioactive Yellow III label only)	Radioactive	172.544

Table 5: General Placard Requirements

Category of material (Hazard class or division number and additional description, as appropriate)	Placard name	Placard Design Section Ref. (§)
1.4	Explosives 1.4	172.523
1.5	Explosives 1.5	172.524
1.6	Explosives 1.6	172.525
2.1	Flammable Gas	172.532
2.2	Non-Flammable Gas	172.528
3	Flammable	172.542
Combustible liquid	Combustible	172.544
4.1	Flammable Solid	172.546
4.2	Spontaneously Combustible	172.547
5.1	Oxidizer	172.550
5.2 (Other than organic peroxide, Type B, liquid or solid, temperature controlled).	Organic peroxide	172.552
6.1 (PG I or II, other than Zone A or B inhalation hazard).	Poison	172.554
6.1 (PG III)	Keep Away from Food	172.553
6.2	(None)	
8	Corrosive	172.558
9	Class 9	172.560
ORM-D	(None)	

8.7 Documentation

Any time demolition material or MEC are being transported, this chapter to include the completed copies of documents described below will be in the vehicle.

- Instructions for Motor Vehicle owners (Emergency Response Information) - Figure 6.
    - Only those items, which are being transported, will be entered in the form with the applicable qty/units and weight columns completed. It is imperative that the NEW limitations of 55 lbs not be exceeded. All required data will be entered on the front and the Guide 50 block should be checked on the back of the form.
- Explosives Purchase/Receipt/Transport Authorization List - Figure 1
    - The form will be completed ensuring the pertinent data for all those transporting explosives is included on the form. As with the other required forms, this one will be part of the transport paperwork. Only the route shown will be used unless there is an emergency or the route is blocked.

- Any deviation from the planned route will be reported to and coordinated with the UXOSO.

- Motor Vehicle Inspection Checklist - Figure 7.
    - The form is to be completed prior to placing any explosives in the vehicle and will accompany the shipment.

- BATF Permit/License.
    - A copy of the current BATF license will accompany the vehicle and be readily available.

9.0 FIRE PROTECTION PLAN

9.1 Explosive Storage Area (ESA)

In the event of a fire at or near the ESA, all site personnel will be evacuated to a distance outside the approved Inhibited Building Distance (IBD), as stated in Chapter 4, of the approved Site Work Plan. An honest attempt to fight the fire will be made with all available fire-fighting equipment on hand. A reasonable decision will be made by the UXOSO when these means have been exhausted and any further attempts will endanger site personnel. At no time will anyone attempt to evacuate the explosives from the ESA; should the bunker door be open at the time, it will be shut and secured if time permits.

The UXOSO will meet the responding local fire department and brief them on the following –

- Total Quantity of Explosives, by hazard classification, inside the ESA
- Time the fire started
- The amount of time the bunkers have been engulfed by flames

All spark emitting devices, matches and flame producing items will not be carried into the ESA. These items will be left outside in a designated location.

9.2 General Housekeeping

Periodic housekeeping (bi-weekly or as needed) will be conducted around and in the ESA. Vegetation will be cut and maintained to a level that will not propagate the spread of a fire. All trash will be removed from the fencing around the ESA.

Figure 7 - Explosive Vehicle Inspection Form

EXPLOSIVE VEHICLE INSPECTION FORM			
This form must be filled out for any vehicle carrying explosives, prior to loading.			
DRIVERS NAME		LICENSE NUMBER	
COMPANY			
TYPE OF VEHICLE		VEHICLE NUMBER	
INSPECTION DATE/TIME		INSPECTOR	
PART INSPECTED	**SAT.**	**UNSAT.**	**COMMENT**
HORN			
STEERING SYSTEM			
WIPERS			
MIRRORS			
FIRE EXTINGUISHERS (10 ABC, 2 EACH)			
REFLECTORS			
EMERGENCY FLASHERS			
LIGHTS			
ELECTRIC WIRING			
FUEL SYSTEM			
EXHAUST SYSTEM			
BRAKE SYSTEM			
SUSPENSION			
CARGO SPACE			
TIRES, WHEELS, RIMS			
TAILGATE			
TARPAULIN			
INSPECTION RESULTS (INSPECTOR INITIAL)			
ACCEPTED:			
REJECTED:			
REMARKS			
DRIVERS SIGNATURE/DATE			INSPECTORS SIGNATURE/DATE

Attachment 1

Material Data Sheets

CORD DETONATING (1.4D) (UN0289)

New Explosive Weight (New)

FORMULA: .00229 OZ = 1 Grain
80 gr. X .00229 = .1832 oz.
.1832 oz. Per ft. x 100' = 18.32 oz. Total Net Explosive Weight / 100 feet

HAZARDOUS CLASS OF US MILITARY EXPLOSIVES AND MUNITIONS

Proper Shipping Name:
CORD DETONATING, FLEXIBLE UN0289 1.4D

CFR 49 172.101 TABLE OF HAZMAT MATERIAL
CORD DETONATING, FLEXIBLE UN0289 1.4D

CFR 49 173.63 (a)

Packaging Exceptions

(a) Cord, Detonating (UN0065), having an explosive content not exceeding 6.5g (0.23 ounces) per 30 centimeter length (one linear foot) may be offered for transportation domestically and transported as Cord, detonating (UN0289), Division 1.4 Compatibility Group D (1.4D) explosives, if the gross weight of all packages containing Cord, detonating (UN0065), does not exceed 45 kg (99 pounds) per:

(1) Transport vehicle, freight container, or cargo-only aircraft;

UN0065 and UN0289 Use Packaging Instruction #139
Research and Special Programs Administration, DOT § 173.62

Packing Instruction	Inner Packagings	Intermediate Packagings	Outer Packagings
139 ..... PARTICULAR PACKING REQUIREMENTS OR EXCEPTIONS: 1. For UN 0065, 0102, 0104, 0289 and 0290, the ends of the detonating cord must be sealed, for example, by a plug firmly fixed so that the explosive cannot escape. The ends of CORD DETONATING flexible must be fastened securely. 2. For UN 0065 and UN 0289, inner Packagings are not required when they are fastened securely in coils.	Bags ..... Plastics Receptacles ..... Fiberboard Metal Plastics Wood Reels ..... Sheets ..... Paper Plastics	Not necessary	Boxes. Steel (4A). Aluminum (4B). Wood, natural, ordinary (4C1). Wood, natural, sift proof walls (4C2). Plywood (4D). Reconstituted wood (4F). Fibreboard (4G). Plastics, solid (4H2). Drums. Steel, removable head (1A2). Aluminum, removable head (1B2). Plywood (1D). Fibre (1G). Plastics, removable head (1H2).

SHAPE CHARGE (1.4S) (UN0441)

HAZARDOUS CLASS OF US MILITARY EXPLOSIVES AND MUNITIONS

Proper Shipping Name:

CHARGES, SHAPED, COMMERCIAL W/O DETONATOR UN0441 1.4S

CFR 49 172.101 TABLE OF HAZMAT MATERIAL

CHARGERS, SHAPED, COMMERCIAL WITHOUT DETONATOR UN0441 1.4S

CFR 49 173.62

Packaging & Instructions #137

49 CFR ch. 1 (10-97 Edition) § 173.62

Packing Instruction	Inner Packagings	Intermediate Packagings	Outer Packagings
137 ..... PARTICULAR PACKING REQUIREMENTS OR EXCEPTIONS: For UN 0059, 0439, 0440, and 0441, when the shaped charges are packed singly, the conical cavity must face downwards and the package marked "This Side Up". When the shaped charges are packed in pairs, the conical cavities must face inwards to minimize the jetting effect in the event of accidental initiation. 2. For UN 0065 and UN 0289, inner Packagings are not required when they are fastened securely in coils.	Bags ..... Plastics Boxes ..... Fiberboard Tubes ..... Fiberboard Metal Plastics Dividing partitions in the outer Packagings.	Not necessary ...	Boxes. Steel (4A). Aluminum (4B). Wood, natural, ordinary (4C1). Wood, natural, sift proof walls (4C2). Plywood (4D). Reconstituted wood (4F). Fibreboard (4G).

DETONATOR, NON-ELECTRIC (1.4B) (UN0267)

HAZARD CLASSIFICATION OF US MILITARY EXPLOSIVES AND MUNITIONS

Proper Shipping Name

DETONATOR, NON-ELECTRIC UN0267 1.4B

CFR 49 172.101 TABLE OF HAZARDOUS MATERIALS

DETONATOR, NON-ELECTRIC UN0267 1.4B

Special Provisions (column #7)

#103 Detonators which will not mass detonate and undergo only limited propagation in the shipping package may be assigned to 1.4B classification code. Mass detonate means that more than 90 percent of the devices tested in a package explode practically simultaneously.

CFR 49 173.63 (g)

Packaging Exceptions

(g) Detonators that are classed as 1.4B or 1.4S and contain no more than 1 g of explosive (excluding ignition and delay charges) may be packed as follows in which case they are excepted from the packaging requirements of § 173.62:

(1) No more than 50 detonators in one inner packaging;

(2) IME Standard 22 container is used as the outer packaging;

(3) No more than 1000 detonators in one outer packaging; and

(4) Each inner packaging is marked "1.4B Detonators" or "1.4S Detonators", as appropriate.

DETONATOR, ELECTRIC (1.4B) (UN0244)

HAZARDOUS CLASSIFICATION OF US MILITARY EXPLOSIVES AND MUNITIONS

Proper Shipping Name

DETONATOR, ELECTRIC UNO244 1.4B

CFR 49 172.101 TABLE OF HAZARDOUS MATERIALS

DETONATOR, ELECTRIC UN0255 1.4B

Special Provisions (column #7)

#103 Detonators which will not mass detonate and undergo only limited propagation in the shipping package may be assigned to 1.4B classification code. Mass detonate means that more than 90 percent of the devices tested in a package explode practically simultaneously. Limited propagation means that if one detonator near the center of a shipping package is exploded, the aggregate weight of explosives, excluding ignition and delay charges, in this and all additional detonators in the outside packaging that explode may not exceed 25 grams.

CFR 49 173.63 (f) & (g)

Packaging exceptions:

(f) Detonators containing no more than 1g explosive (excluding ignition and deadly charges) that are electric blasting caps with leg wires four feet long or longer, delay connectors in plastic sheaths, or blasting caps with empty plastic tubing twelve feet long or longer, may be packed as follows, in which case they are excepted from the packaging requirements of § 173.62:

(1) No more than 50 detonators in one inner packaging;
(2) IME Standard 22 container or compartment is used as the outer packaging;
(3) No more than 1,000 detonators in one outer packaging; and
(4) No material may be loaded on top of the IME Standard 22 container and no material may be loaded against the outside door of the IME standard 22 compartment.

(g) Detonators that are classed as 1.4B or 1.4S and contain no more than 1g of explosive (excluding) ignition and delay charges) may be packed as follows in which case they are excepted from the packaging requirements of § 173.62:

(1) No more than 50 detonators in one inner packaging;
(2) IME Standard 22 container is used as the outer packaging;
(3) No more than 1,000 detonators in one outer packaging; and
(4) Each inner packaging is marked "1.4B Detonators" or "1.4S Detonators", as appropriate.

CFR 49 173.62 SPECIAL PACKING REQUIREMENTS FOR EXPLOSIVES
(Explosives Table) UN0267 PI# 131

Research and Special Programs Administration, DOT § 173.62

Table of Packing Methods - Continued

Packing Instruction	Inner Packagings	Intermediate Packagings	Outer Packagings
131 ..... PARTICULAR PACKING REQUIREMENTS OR EXCEPTIONS: 1. For UN 0029, 0267, and 0455, bags and reels may not be used as inner packagings. 2. For UN 0030, 0255, and 0455, inner packagings are not required when detonators are packed in pasteboard tubes, or when their leg wires are wound on spools with the caps either placed inside the spool or securely taped to the wire on the spool, so as to restrict freedom of movement of the caps and to protect them from impact forces. 3. For UN 0360, 0361, and 0500, detonators are not required to be attached to the safety fuse, metal-clad mild detonating cord, detonating cord, or shock tube, inner packagings are not required if the packing configuration restricts freedom of movement of the caps and protects them from impact forces.	Bags ..... Paper Plastics Receptacles ..... Fiberboard Metal Plastics Wood Reels	Not necessary ...	Boxes. Steel (4A). Aluminum (4B). Wood, natural, ordinary (4C1). Wood, natural, sift proof walls (4C2). Plywood (4D). Reconstituted wood (4F). Fibreboard (4G). Drums. Steel, removable head (1A2). Aluminum, removable head (1B2). Fibre (1G). Plastics, removable head (1H2).

CFR 49 173.63 PA PACKAGING EXCEPTIONS (Enclosure 1)
(g) (2) IME Standard 22 container
Publication: Institute of Makers of Explosives SLP #22 May 1993
Publication: Guide for the Use of the IME 22 Container Oct. 1, 1993

IGNITER, M2/M60 F/TIME BLASTING FUSE (1.4S) (UN0131)

HAZARD CLASSIFICATION OF US MILITARY EXPLOSIVES AND MUNITIONS

Proper Shipping Name:

LIGHTERS, FUSE 1.4S UN0131

CFR 172.101 TABLE OF HAZARDOUS MATERIALS

LIGHTER, FUSE 1.4S UN0131

CFR 173.62

Packaging Instruction #142

49 CFR ch. 1 (10-97 Edition) § 173.62

Table of Packing Methods - Continued

Packing Instruction	Inner Packagings	Intermediate Packagings	Outer Packagings
142	Bags ..... Paper Plastics Receptacles ..... Fiberboard Metal Plastics Wood Sheets ..... Paper Trays, fitted with dividing partitions plastics	Not necessary ...	Boxes. Steel (4A). Aluminum (4B). Wood, natural, ordinary (4C1). Wood, natural, sift proof walls (4C2). Plywood (4D). Reconstituted wood (4F). Fibreboard (4G). Plastics, solid (4H2). Drums. Steel, removable head (1A2). Aluminum, removable head (1B2). Fibre (1G). Plastics, removable head (1H2).

FUSE, BLASTING TIME M700 (1.4S) (UN0105)

HAZARD CLASSIFICATION OF US MILITARY EXPLOSIVES AND MUNITIONS

Proper Shipping Name:

FUSE, SAFETY UN0105 1.4S

CFR 49 172.101 TABLE OF HAZARDOUS MATERIALS

FUSE, SAFETY UN0105 1.4S

CFR 49 173.62

Packing Instructions #140

Research and Special Programs Administration, DOT § 173.62

Table of Packing Methods - Continued

Packing Instruction	Inner Packagings	Intermediate Packagings	Outer Packagings
140 ..... PARTICULAR PACKING REQUIREMENTS OR EXCEPTIONS: 1. If the ends of UN 0104 are sealed, no inner packagings are required. 2. For UN 0101, the packaging must be sift-proof except when the fuse is covered by a paper tube and both ends of the tube are covered with removable caps. 3. For UN 0101, steel or aluminum boxes or drums must not be used.	Bags ..... Plastics Reels ..... Sheets ..... Paper, kraft Plastics	Not necessary ...	Boxes. Steel (4A). Aluminum (4B). Wood, natural, ordinary (4C1). Wood, natural, sift proof walls (4C2). Plywood (4D). Reconstituted wood (4F). Fibreboard (4G). Plastics, solid (4H2). Drums. Steel, removable head (1A2). Aluminum, removable head (1B2). Fibre (1G).

Attachment 2

Motor Vehicle Inspection
DoD Form 626

MOTOR VEHICLE INSPECTION (TRANSPORTING HAZARDOUS MATERIALS)

(Read Instructions before completing this form.)

This form applies to all vehicles which must be marked or placarded in accordance with Title 49 CFR.	1. GOVERNMENT BILL OF LADING/TRANSPORTATION CONTROL NUMBER

SECTION 1 - DOCUMENTATION	ORIGIN a.	DESTINATION b.
2. CARRIER/GOVERNMENT ORGANIZATION		
3. DATE/TIME OF INSPECTION		
4. LOCATION OF INSPECTION		
5. OPERATOR(S) NAME(S)		
6. OPERATOR(S) LICENSE NUMBER(S)		
7. MEDICAL EXAMINER'S CERTIFICATE*		

8. (X if satisfactory at origin)

a. MILITARY HAZMAT ENDORSEMENT		d. ERG OR EQUIVALENT COMMERCIAL:		YES		NO		9. CVSA DECAL DISPLAYED ON COMMERCIAL EQUIPMENT*	YES / NO
b. VALID LEASE*		e. DRIVER'S VEHICLE INSPECTION REPORT*						a. TRUCK/TRACTOR	
c. ROUTE PLAN		f. COPY OF 49 CFR PART 397						b. TRAILER	

SECTION 11 - MECHANICAL INSPECTION

All items shag be checked on empty equipment prior to loading. Items with an asterisk shag be checked on all incoming loaded equipment.

10. TYPE OF VEHICLE(S)	1 1. VEHICLE NUMBER(S)

12. PART INSPECTED *(X as applicable)*	ORIGIN (1) SAT	ORIGIN (1) UNSAT	DESTINATION (2) SAT	DESTINATION (2) UNSA I		ORIGIN (1) SAT	ORIGIN (1) UNSAT	DESTINATION (2) SAT	DESTINATION (2) UNSAT	COMMENTS (3)
a. SPARE ELECTRICAL FUSES					k EXHAUST SYSTEM					
b. HORN OPERATIVE					1. BRAKE SYSTEM*					
c. STEERING SYSTEM					rn. SUSPENSION					
d. WINDSHIELD/WIPERS					n. COUPLING DEVICES					
e. MIRRORS					o. CARGO SPACE					
f. WARNING EQUIPMENT					p. LANDING GEAR*					
g. FIRE EXTINGUISHER*					q. TIRES, WHEELS, RIMS					
h. ELECTRICAL WIRING					r. TAILGATE/DOORS*					
i. LIGHTS AND REFLECTORS					s. TARPAULIN*					
j. FUEL SYSTEM*					t. OTHER (Specify)					

13. INSPECTION RESULTS (X *one)* ACCEPTED ☐ REJECTED ☐

(If rejected give reason under "Remarks ". Equipment will be approved if deficiencies are corrected prior to loading.)

14. SATELLITE MOTOR SURVEILLANCE SYSTEM: (X *one)* ACCEPTED ☐ REJECTED ☐

15. REMARKS

16. INSPECTOR SIGNATURE *(Origin)*	17. INSPECTOR SIGNATURE *(Destination)*

SECTION III - POST LOADING INSPECTION

This section applies to Commercial and Govern ment/Military vehicles. All items will be checked prior to release of loaded equipment and shall be checked on all incoming loaded equipment.

	ORIGIN (1) SAT	ORIGIN (1) UNSAT	DESTINATION (2) SAT	DESTINATION (2) UNSAT	COMMENTS (3)
18. LOADED IAW APPLICABLE SEGREGATION/COMPATIBILITY TABLE OF 49 CIFIR					
19. LOAD PROPERLY SECURED TO PREVENT MOVEMENT					
20. SEALS APPLIED TO CLOSED VEHICLE; TARPAULIN APPLIED ON OPEN EQUIPMENT					
21. PROPER PLACARDS APPLIED					
22. SHIPPING PAPERS/DD FORM 836 FOR GOVERNMENT VEHICLE SHIPMENTS					
23. COPY OF DID FORM 626 FOR DRIVER					
24. SHIPPED UNDER DOT EXEMPTION 868					

25. INSPECTOR SIGNATURE *(Origin)*	26. DRIVER(S) SIGNATURE *(Origln)*
27. INSPECTOR SIGNATURE *(Destination)*	28. DRIVER(S) SIGNATURE *(Destination)*

INSTRUCTIONS

SECTION I - DOCUMENTATION

General Instructions.

All items (2 through 9) will be checked at origin prior to loading. Items with an asterisk (*) apply to commercial operators or equipment only. Only Items 2 through 7 are required to be checked at destination.

Items 1 through 5. Self explanatory.

Item 6. Enter operator's Commercial Driver's License (CDL) number or Military OF-346 License Number. CDL and OF-346 must have the HAZMAT and other appropriate endorsements IAW Part 383.

Item 7. *Enter the expiration date listed on the Medical Examiner's Certificate.

Item 8.a. APPLIES TO MILITARY OPERATORS ONLY. Military Hazardous Materials Certification. In accordance with applicable service regulations, ensure operator has been certified to transport hazardous materials.

b. *Valid Lease. Shipper will ensure a copy of the appropriate contract of lease is carried in all leased vehicles and is available for inspection. (Defense Transportation Regulation (DTR) requirement.)

c. Route Plan. Prior to loading any Hazard Class/Division 1 . 1 , 1 .2, or 1 .3 (Explosives) for shipment, ensure that the operator possesses a written route plan in accordance with 49 CFR Part 397. Route Plan requirements for Hazard Class 7 (Radioactive) materials are found in 49 CFR 397. 1 0 1.

d. Emergency Response Guidebook (ERG) or Equivalent. Commercial operators must be in possession of an ERG or equivalent document. Shipper will provide applicable ERG page(s) to military operators.

e. *Driver's Vehicle Inspection Report. Review the operator's Vehicle Inspection Report. Ensure that there are no defects listed on the report that would affect the safe operation of the vehicle.

f. Copy of 49 CFR Part 397. Operators are required by regulation to have in their possession a copy of 49 CFR Part 397 (Hazardous Materials Driving and Parking Rules). If military operators do not possess this document, shipper may provide a copy to operator.

Item 9. *Commercial Vehicle Safety Alliance (CVSA) Decal. Check to see if equipment has a current CVSA decal and mark applicable box. Vehicles without CVSA, check documentation of the last vehicle periodic inspection.

SECTION 11 - MECHANICAL INSPECTION

General Instructions.

All items (12.a. through 12.t.) will be checked on all incoming empty equipment prior to loading. All UNSATISFACTORY conditions must be corrected prior to loading. Items with an asterisk (*) shall be checked on all incoming loaded equipment. Unsatisfactory conditions that would affect the safe off-loading of the equipment must be corrected prior to unloading.

SECTION 11 *(Continued)*

Item 12.a. Spare Electrical Fuses. Check to ensure that at least one spare fuse for each type of installed fuse is carried on the vehicle as a spare or vehicle is equipped with an overload protection device (circuit breaker). (49 CFR 393.95)

b. Horn Operative. Ensure that horn is securely mounted and of sufficient volume to serve purpose. (49 CFR 393.8 1)

c. Steering System. The steering wheel shall be secure and must not have any spokes cracked through or missing. The steering column must be securely fastened. Universal joints shall not be worn, faulty or repaired by welding. The steering gear box shall not have loose or missing mounting bolts or cracks in the gear box mounting brackets. The pitman arm on the steering gear output shaft shall not be loose. Steering wheel shall turn freely through the limit of travel in both directions. All components of a power steering system must be in operating condition. No parts shall be loose or broken. Belts shall not be frayed, cracked or slipping. The power steering system shall not be leaking. (49 CFR 396 Appendix G)

d. Windshield/Wipers. Inspect to ensure that windshield is free from breaks, cracks or defects that would make operation of the vehicle unsafe; that the view of the driver is not obscured and that the windshield wipers are operational and wiper blades are in serviceable condition. Defroster must be operative when conditions require. (49 CFR 393.60, 393.78 and 393.79)

e. Mirrors. Every vehicle must be equipped with two rear vision mirrors located so as to reflect to the driver a view of the highway to the rear along both sides of the vehicle. Mirrors shall not be cracked or dirty. (49 CFR 393.80)

f. Warning Equipment. Equipment must include three bidirectional emergency reflective triangles that conform to the requirements of FMVSS No. 125. FLAME PRODUCING DEVICES ARE PROHIBITED. (49 CFR 393.95)

g. Fire Extinguisher. Military vehicles must be equipped with two serviceable fire extinguishers with an Underwriters Laboratories rating of 10 BC or more. (Commercial motor vehicles must be equipped with one serviceable 10 BC Fire Extinguisher). Fire extinguisher(s) must be located so that it is readily accessible for use and securely mounted on the vehicle. The fire extinguisher must be designed, constructed and maintained to permit visual determination of whether it is fully charged. (49 CFR 393.95)

h. Electrical Wiring: Electrical wiring must be clean and properly secured. Insulation must not be frayed, cracked or otherwise in poor condition. There shall be no uninsulated wires, improper splices or connections. Wires and electrical fixtures inside the cargo area must be protected from the lading. (49 CFR 393.28, 393.32, 393.33)

SECTION 11 *(Continued)*

i. Lights/Reflectors. (Head, tail, turn signal, brake, clearance, marker and identification lights, Emergency Flashers). Inspect to see that all lighting devices and reflectors required are operable, of proper color and properly mounted. Ensure that lights and reflectors are not obscured by dirt or grease or have broken lenses. High/Low beam switch must be operative. Emergency Flashers must be operative on both the front and rear of vehicle. (49 CFR 393)

j. Fuel System. Inspect fuel tank and lines to ensure that they are in serviceable condition, free from leaks, or evidence of leakage and securely mounted. Ensure that fuel tank filler cap is not missing. Examine cap for defective gasket or plugged vent. Inspect filler necks to see that they are in completely serviceable condition and not leaking at joints. (49 CFR 393.83 and 396 Appendix G)

k. Exhaust System. Exhaust system shall discharge to the atmosphere at a location to the rear of the cab or if the exhaust projects above the cab, at a location near the rear of the cab. Exhaust system shall not be leaking at a point forward of or directly below the driver compartment. No part of the exhaust system shall be located where it will burn, char or damage electrical wiring, fuel system or any other part of the vehicle. No part of the exhaust system shall be temporarily repaired with wrap or patches. (49 CFR 393.83 and 396 Appendix G)

1. Brake System (to include hand brakes, parking brakes and Low Air Warning devices). Check to ensure that brakes are operational and properly adjusted. Check for audible air leaks **around air brake components and air lines. Check for fluid leaks, cracked or damaged lines in hydraulic brake systems. Ensure that parking brake is operational and properly adjusted. Low Air Warning devices must be operative. (49 CFR 396 Appendix G)**

m. Suspension. Inspect for indications of misaligned, shifted or cracked springs, loosened shackles, missing bolts, spring hangers unsecured at frame and cracked or loose U-bolts. Inspect for any unsecured axle positioning parts, and sign of axle misalignment, broken torsion bar springs (if so equipped). (49 CFR 396 Appendix G)

n. Coupling Devices (Inspect without uncoupling). Fifth Wheels: Inspect for unsecured mounting to frame or any missing or damaged parts. Inspect for any visible space between upper and lower fifth wheel plates. Ensure that the locking jaws are around the shank and not the head of the kingpin. Ensure that the release lever is seated properly and safety latch is engaged. Pintle Hook, Drawbar, Towbar Eye and Tongue and Safety Devices: Inspect for unsecured mounting, cracks, missing or ineffective fasteners (welded repairs to pintle hook is prohibited). Ensure safety devices (chains, hooks, cables) are in serviceable condition and properly attached. (49 CFT 396 Appendix G)

o. Cargo Space. Inspect to ensure that cargo space is clean and free from exposed bolts, nuts, screws, nails or inwardly projecting parts that could damage the lading. Check floor to ensure it is tight and free from holes. Floor shall not be permeated with oil or other substances. (49 CFR 177.815(e)(1) and 398.94)

p. Landing Gear. Inspect to ensure that landing gear and assembly are in serviceable condition, correctly assembled, adequately lubricated and properly mounted.

SECTION 11 *(Continued)*

q. Tires, Wheels and Rims: Inspect to ensure that tires are properly inflated. Flat or leaking tires are unacceptable. Inspect tires for cuts, bruises, breaks and blisters. Tires with cuts that extend into the cord body are unacceptable. Thread depth shall not be less than: 4/32 inches for tires on a steering axle of a power unit, and 2/32 inches for all other tires. Mixing bias and radial on the steering axle is prohibited. Inspect wheels and rims for cracks, unseated locking rings, broken, loose, damaged or missing lug nuts or elongated stud holes. (49 CFR 396 Appendix G)

r. Tailgate/Doors. Inspect to see that all hinges are tight in body. Check for broken latches and safety chains. Doors must close securely. (49 CFR 177.835(h))

s. Tarpaulin. If shipment is made on open equipment, ensure that lading is properly covered with fire and water resistant tarpaulin. (49 CFR 177.835(h))

t. Other Unsatisfactory Condition. Note any other condition which would prohibit the vehicle from being loaded with hazardous materials.

Item 14. For AA&E and other shipments requiring satellite surveillance, ensure that the Satellite Motor Surveillance System is operable. Shipper will instruct the driver to send a "test" emergency message to DTTS by having the driver activate the "emergency (panic) button". Shipper will contact DTTS at 1-800-826-0794 to verify that test message was received. Message must be received by DTTS for system to be considered operational.

SECTION III - POST LOADING INSPECTION

General Instructions.

All items will be checked prior to the release of loaded equipment. Shipment will not be released until deficiencies are corrected. All items will be checked on incoming loaded equipment. Deficiencies will be reported in accordance with applicable service regulations.

Item 18. Check to ensure shipment is loaded in accordance with 49 CFR Part 177.848 and the applicable Segregation or Compatibility Table of 49 CFR 177.848.

Item 19. **Check to ensure the load is secured from movement in accordance with applicable service outload drawings.**

Item 20. Check to ensure seal(s) have been applied to closed equipment; fire and water resistant tarpaulin applied on open equipment.

Item 2 1. Check to ensure each transport vehicle has been properly placarded in accordance with 49 CFR Part 172 Subpart F.

Item 22. Check to ensure operator has been provided shipping papers that comply with 49 CFR Part 172 Subpart C. For shipments transported by Government vehicle, shipping paper will be DD Form 836.

Item 23. Ensure operator(s) sign DD Form 626, are given a copy and understand the hazards associated with the shipment.

Item 24. **Applies to Commercial Shipments Only. If shipment is made under DOT Exemption 868, ensure that shipping papers are properly** annotated and copy of Exemption 868 is with shipping papers.

OE SECTOR
Standing Operating Procedure (SOP)

Heavy Equipment Operations

PARSONS
5390 Triangle Parkway, Suite 100
Norcross, Georgia 30092

Revision No. 1
February 2005

1.0 INTRODUCTION

The purpose of this SOP is to provide the minimum procedures and safety and health requirements applicable to the operation of heavy equipment, hereinafter referred to as earth moving machinery (EMM).

2.0 SCOPE

This standing operating procedure (SOP) contains information specific to the operation of EMM. It will include manuals and publications relevant to operation, lubrication and preventive and scheduled maintenance of the EMM that may be leased, purchased or otherwise employed on the site. It is incumbent upon all designated operators to familiarize themselves with this SOP and to periodically review it an effort to remain current with safe EMM operations.

3.0 REFERENCES

Procedures and information contained in this document were obtained from the below listed references:

- USACE EM 385-1-1, Safety and Health Requirements Manual;
- USACE EP 385-1-95a, Basic Safety Concepts and Considerations for Ordnance and Explosives Operations;
- USACE EP 1110-1-18, Engineering and Design;
- OSHA Regulation 29CFR1926, Subpart P, Appendix A and 29CFR1926.652, Subpart P, Appendix F, Safety and Health Requirements for Construction;
- AR 385-55, Prevention of Motor Vehicle Accidents;
- DA Pam 385-16, System Safety Engineering and Management; and
- Parsons I & T Policies and Procedures for Health and Safety

4.0 EMM Operations

4.1 Team Composition

The minimum team make-up will be:

- One qualified operator, either a UXO Technician or Non-UXO trained individual;
- One ground guide, UXO Technician I or II, (the EMM Safety Observer can fill this role and that of safety Observer if conditions permit); and
- One EMM Safety Observer, UXO Technician III.

4.1.1 Team Leader

An UXO Technician III (Team Leader) will serve as the EMM Team Leader and overall Safety Observer, directing the site personnel and equipment during the operation. Depending on the complexity of the operation, he may also serve as the backup guide. The EMM Team Leader will be trained, as a competent person when required. (See paragraph 6-4, this SOP).

4.1.2 Ground Personnel

Team members working on EMM operations will be qualified through non-the-job training (OJT) and will perform such tasks as magnetometer checks, manual excavation and checks of the excavation for UXO items. When using a UXO Tech I for manual excavation, a UXO Technician III must be present to supervise.

4.1.3 Equipment Operators

All site personnel, regardless of affiliation, who operate EMM equipment, will be qualified through documented formal training, equivalent previous employment experience or OJT. Documentation of this training will be kept on file at the site. The operator, when engaged in EMM operations, will perform daily inspection and maintenance functions (See figure 1), or as directed by the operator's manual for that specific equipment.

4.1.4 Use of Non-UXO Personnel

Use of Non-UXO personnel as operators on UXO sites is authorized. There is no requirement for additional safety barriers or shielding during the operation, IAW USACE EP 385-1-95a. When the operation has come within one foot of the UXO item or anomaly being investigated, unless the operator has been designated essential personnel, the Non-UXO operator must move outside the pre-designated Minimum Safe Distance (MSD), until recalled by the EMM UXO Technician III.

4.2 Equipment Procedures

The hazards associated with heavy equipment involve moving parts and exposure to possible pinch points. Safe operating procedures for each type of equipment or activity must be reviewed and followed. Safety protection, including equipment guards, which must not be removed, shall be provided to mitigate this problem. Site personnel operating or working within close proximity to heavy equipment will wear hard hats, eye protection, steel-toed boots, and hearing protection (as necessary).

Heavy equipment used on the site must meet the requirements of OSHA, DOT, and general industry standards. The operator will be responsible for completing daily written inspections of all heavy equipment and provide copies of the inspection as well as required certifications to the Site Manager (SM). All personnel who operate equipment must use any safety devices, such as seat belts, that the equipment is equipped with during operation. All operators will follow the following heavy equipment operating rules:

- Only personnel trained in the operation of heavy equipment are permitted to operate such equipment;

- Personnel may only operate equipment for which they have received training and certification. Trainees may operate heavy equipment, but only under competent supervision;

- Before operating any heavy equipment, the operator must conduct a pre-operational check of the piece of equipment. Brakes, hydraulic lines, light signals, fire extinguishers, fluid levels, steering, tires, horn, and other safety devices will be checked daily and maintained in good working order throughout the duration of its use. If it is found to be unsafe, the operator must report the condition immediately to the appropriate supervisor, and the piece of equipment placed in an unserviceable status until it has been repaired or replaced.

- The operators of heavy equipment will complete a daily inspection form (See Figure 1).

- All heavy equipment will not be backed up unless the vehicle has a reverse signal alarm audible above the surrounding noise level, backup warning lights, or the vehicle is backed up using a ground guide.

- Heavy equipment will be provided with necessary safety equipment including seat belts, roll-over protection, emergency shut-off during roll-over, backup warning lights, and audible alarms as applicable.

- Blades and buckets will be lowered to the ground and parking brakes will be set before shutting off any heavy equipment.

- Special consideration must be given to the proper functioning of tires, horns, lights, batteries, controllers, lift systems (including forks, chains, cable and limit switches), brakes, and steering mechanisms;

- All heavy equipment must be operated at an authorized safe speed, consistent with conditions, and at a safe distance from other vehicles. Heavy equipment must be under positive control at all times;

- No riders other than the driver are permitted on heavy equipment at any point;

- When heavy equipment is left unattended, loads must be lowered, controls neutralized, power shut off, and brakes set. Wheels should be chocked if the equipment is parked on an incline.

- Backhoe support struts (downriggers) shall be equipped with cleated pads for use in soft sandy soil rather than rubber pads (for hard surfaces).

- When working near a backhoe or excavator, field personnel will maintain sight contact with the operator. Field personnel shall not work within the swing radius of the equipment while the equipment is operating. The swing radius will be defined with traffic cones, barrier tape, or other suitable means, such as inscribing the radius on the soil surface using the backhoe bucket.

- Personnel will not cross the demarcated line without first establishing eye contact with the operator. The operator will cease vehicle operations and remove his hands and feet from the controls and/or turn the equipment off, before allowing personnel access to the area within the swing radius. Operations will resume only after all personnel have left the area within the swing radius.

5.0 PERSONNEL PROTECTIVE EQUIPMENT (PPE)

Modified Level D PPE will be required for personnel engaged in EMM operations. Clothing items will be:

- Coveralls or work clothing as prescribed by APP;
- Work gloves, leather or canvas, as prescribed by APP;
- Safety glasses - as wind conditions and airborne particulate matter dictates;
- Hardhats;
- Highly Visible Safety Vests;
- Work Boots, steel toe - Sturdy and of sufficient height to aid in ankle support;
- Hearing Protection - Will be determined through a Noise Survey (Sound Level Meter) for any EMM equipment brought on site. Until the survey is completed and the degree of attenuation determined, personnel on the EMM team will wear appropriate hearing protection; and
- Dust Masks - as wind conditions and airborne particulate matter dictates.

NOTE: *If the EMM equipment is being used for the clearance in support of other operations, PPE will be IAW that specific matrix (i.e. rat nests - Hantavirus SOP or RCWM projects).*

6.0 GENERAL SAFETY PRECAUTIONS

6.1.1 Underground Utilities

Utilities companies shall be contacted within established or customary local response times advised of the proposed work and asked to locate underground utilities (sewer, telephone, electric, water, gas or any other utility) prior to start of actual excavation. When these locations cannot be established, the excavation may proceed, provided the EMM operation does so with caution, and only after site personnel, using detection equipment, have made an attempt to locate utilities. While the excavation is opened, and underground utilities exposed, they shall be protected, supported or removed as necessary to safeguard workers.

6.1.2 Exposure to Vehicle Traffic

EMM team members exposed to vehicular traffic shall be provided and wear warning vests or other suitable garment with a highly visible (reflector) material. Traffic direction paddles or saw horse type barricades may also be required to halt or redirect vehicular traffic around the excavation site.

6.1.3 Exposure to Falling Loads

No worker shall be permitted underneath loads handled by lifting or digging equipment. Workers are required to stand away from any vehicle being loaded or unloaded to avoid being struck by any spillage or falling material.

6.1.4 Equipment Warning Device

All EMM equipment will be equipped with an audile warning system that sounds when the equipment is backing up. EMM equipment needing to be moved adjacent to an excavation or approach the edge, and the operator does not have a clear and direct view of the edge, will institute a warning system, such as barricades, stop logs or arm and hand signals from the safety observer.

6.1.5 Loose Rock or Soil

Workers will be protected from excavated or other materials or equipment that could pose a hazard by falling or rolling into excavations. All equipment or materials will be placed at least 2 feet (.61m) from the edge of excavations, or by use of retaining devices that are sufficient to prevent the equipment or material from falling or rolling into the excavation. Also scaling the excavation face to remove loose rock or soil and the installation of protective barriers at intervals on the face to stop or contain falling material will be used when appropriate.

6.1.6 Cave-In

Excavations will be protected from cave-ins by adequate protective systems (sloping and benching or shielding and support).

6.1.7 Operation of EMM

EMM will not be operated without a spotter. This includes moving, repositioning, and using the front and rear attachments. Prior to starting an excavation, a safety arc will be etched in the ground with the front or rear boom, fully extended. If operating on a hard surface, the safety arc will be marked on the ground, with bright spray paint. Prior to anyone entering the safety arc, the operator will:

- Swing the boom fully to one side;
- Lower the bucket to the ground;
- Place engine in idle speed; and
- Hold his hands clear of the controls or in the “Hands Up” position.

6.2 UXO Precautions

All EMM operations will adhere to the MSD as described in the site Work Plan. The lateral distances will be maintained when conducting EMM operations on a UXO site. These distances may be reduced or extended by the USACE Site Safety Representative, based on an assessment of site history, size of site, expected UXO, terrain features or other such factors that may apply. The following distances shall apply as applicable:

- 200 feet minimum or the K-50 factor distance (whichever is greater) from non-UXO trained site personnel, unrelated to the operation.

- 200 feet minimum or the K-50 factor distance (whichever is greater) from another EMM operation or other manual intrusive operations.

- All EMM excavations will be conducted offset laterally for the suspected UXO item or anomaly being investigated.

- The EMM will uncover no more than six (6) inches of earth per dig.

- The EMM will not be used to excavate closer than 12 inches from UXO.

- Suspend all operations immediately upon approach of an electrical storm.

- Observe the hazards of electromagnetic radiation (EMR) precautions when working in the vicinity of electrically initiated or susceptible UXO.

- Do not handle any MEC unnecessarily.

- Incorporate appropriate property protective measures for shock and fragmentation when conducting MEC operations.

6.3 Equipment Safety Precautions

All EMM operators will conduct familiarization and OJT with the EMM equipment prior to any excavation operation. All EMM equipment on site will have:

- Roll-Over Protection (ROP) and certificate on file at site.

- Back-up Warning System.

- 5A:BC fire extinguisher.

- Site Radio.

- Operator's Manual and Lubrication Order.

6.4 Training

6.4.1 Competent Person

The EMM Team Leader will serve, as the "Competent Person", for all EMM operations. The Project Health and Safety Officer (PHSO) or the OE Group Certified Industrial Hygienist (CIH) will conduct this training, during the site specific training. This training will be documented and kept on file at the site. Minimum elements of training will include:

- Review of OSHA Regulation for Safety and Health Requirement for Construction/Excavations – *OSHA Regulation 29CFR1926, Subpart P, Appendix A and 29CFR1926.652, Subpart P, Appendix F,* (Annex A of this SOP)

- Proper Shoring and Sloping Techniques
- Soil classification and evaluation at the excavation site.
- Responsibilities of a Competent Person.

Heavy Equipment Inspection Report

Date:	**Vehicle Make:**	**Rental/Lease/Private** *(circle one)*
Lic Plate #:	**Veh VIN#:**	
Starting Mileage/Hours for Week:	**Ending Mileage/Hours for Week:**	

General Vehicle Inspection

Check { } with R for repair needed; X for OK; / for adjustment made

1. Windshield { }	**3. Vehicle Interior { }**
2. Vehicle Exterior { }	**4. Leaks { }**
5. Lights: a. Headlights { } d. Brake Lights { } b. Tail lights { } e. Back-up Alarm { } c. Turn Signals { }	
6. Brakes { }	**10. Belts { }**
7. Horn { }	**11. Defroster { }**
8. Tires/Tracks (Tread wear/pressure) { }	**12.Radiator/Hoses** (DON'T check when hot) { }
9. Windshield Wipers/Washer { }	**13. Battery { }**
14. Fluid Levels: (Circle approximate level) a. Oil Full 1qt low Added_____ b. Coolant: Full Need coolant Added_____ c. Transmission: Full 1pt low Added_____ d. Fuel: Full ½ ¼ Empty	e. Hydraulic Fluid Full 1qt low Added_____ f. Grease Fittings Full Added_____ g. ROPS Certificate Yes No
Comments/Repairs/Service(s) Needed: Next Service @_____hrs	

Figure 1

Annex A

Soil Classification for EMM Operations

1.0 Soil Types

The following soil types may be encountered in the course of excavating soil. A knowledge of soil characteristics of the soil types is beneficial to understanding the hazards associated with each.

- **Cemented Soil** – A soil in which a chemical agent, such as calcium carbonate, holds the particles together whereas a hand-size sample cannot be crushed into powder or individual soil particles by finger pressure.

- **Cohesive Soil** – A fine grained soil (clay) or soil with a high clay content, which has cohesive strength. Cohesive soil does not crumble, can be excavated with vertical side-slopes and is "plastic" when moist. Cohesive soil is hard to break up when dry, and exhibits significant cohesion when submerged. Cohesive soils include clayey silt, sandy clay, silty clay, clay and organic clay.

- **Dry Soil** – A soil that does not exhibit visible signs of moisture content.

- **Fissured Soil** – A soil material that has a tendency to break along definite planes of fracture with little resistance or a material that exhibits open cracks, such as "tension cracks", in an exposed surface.

- **Granular Soil** – Means gravel, sand, or silt (coarse grained soil) with little or no clay content. Granular soil has no cohesive strength. Some moist granular soils exhibit apparent cohesion. Granular soil cannot be molded when moist and crumbles easily when dry.

- **Layered System** – Means two or more distinctly different soil or rock types arranged in layers. Micaceous seams or weakened planes in rock or shale are considered layered.

- **Moist Soil** – Means a condition in which a soil looks and feels damp. Moist cohesive soils can easily be shaped into a ball and rolled into small diameter threads before crumbling. Moist granular soil that contains some cohesive material will exhibit signs of cohesion between particles.

- **Plastic Soil** – means a property of a soil, which allows the soil to be deformed or molded without cracking, or appreciable volume change.

- **Saturated Soil** – Means a soil in which the voids are filled with water. Saturation does not require flow. Saturation, or near saturation, is necessary for the proper use of instruments such as a penetrometer or sheer vane.

2.0 Soil classification

If personnel are to enter the excavation, the soils of the excavation must be classified to determine the design of the appropriate protective system. Each soil and rock deposit at an excavation site must be classified by a competent person, as either stable rock, Type A, Type B, or Type C soil.

The soil classification results must be made based on the results of at least one visual test (tension cracks or signs that the soil has been previously disturbed) and one manual test (use of pocket penetrometer or shear-vane to measure unconfined compression strength). The definitions of the various soil classifications are presented below.

- **Stable Rock** is natural solid mineral matter that can be excavated with vertical sides and will remain intact while exposed.
- **Type A Soils** are cohesive soils with an unconfined compressive strength of 1.5 tons per square foot (tsf) (144 kPa) or greater. Examples of Type A cohesive soils are: clay, silty clay, sandy clay, clay loam and, in some cases, silty clay loam and sandy clay loam. A soil cannot be classified as Type A if it is fissured; subject to vibration from traffic, pile driving, or similar effects; has previously been disturbed, is part of a sloped, layered system where the layers dip into the excavation on a slope of 4 horizontal to 1 vertical (4H:1V) or greater; or has seeping water.
- **Type B Soils** are cohesive soils with an unconfined compressive strength greater than 0.5 tsf (48 kPa) but less than 1.5 tsf (144 kPa). Examples of other Type B soils are: angular gravel; silt; silt loam; previously disturbed soils unless otherwise classified as Type C; soils that meet the unconfined compressive strength or cementation requirements of Type A soils but are fissured or subject to vibration; dry unstable rock; and layered systems sloping into the trench at a slope less than 4H:1V (only if the material would be classified as a Type B soil).
- **Type C Soils** are cohesive soils with an unconfined compressive strength of 0.5 tsf (48 kPa) or less. Other Type C soils include: granular soils such as gravel, sand and loamy sand, submerged soil, soil from which water is freely seeping, and submerged rock that is not stable. Also included in this classification is material in a sloped, layered system where the layers dip into the excavation or have a slope of four horizontal to one vertical (4H:1V) or greater.

Table 1-1
Maximum Allowable Slopes

Soil or Rock Type	**Maximum Allowable Slopes (H:V) for Excavations less than 20 feet in depth**
Stable Rock	Vertical (90 deg.)
Type A	¾:1 (53 deg)
Type B	1:1 (45 deg)
Type C	1 ½:1 (34 deg)

Exception: Simple slope excavations, which are open 24 hours, or less (short term) and 12 feet or less in depth shall have a maximum allowable slope of ½:1.

Annex B

Refresher Examination for EMM Operations

EMM EQUIPMENT REFRESHER EXAM

LOCATION_____

NAME_____DATE_____

ORGANIZATION_____

Circle the correct answer or fill in the blank

1. When performing preventive/pre-operational maintenance on EMM equipment, with out a lubrication chart, where should you look for grease fittings?

a. Behind the wheels.
b. At every pivot point.
c. On the bucket teeth.
d. At a local service station.

2. Before starting to excavate what should you check for?

a. Underground utilities.
b. Overhead utilities.
c. Endangered wildlife habitats and vegetation, as outlined in the Work Plan.
d. All the above.

3. ROPS stands for?

a. Read Operational Standards.
b. Round Off Posts Stops.
c. Roll Over Protection System.
d. Roll Or Push Slowly.

4. According to Corps Safety Concepts how close can you excavate to UXO?

a. 6”.
b. 1’.
c. 1 ½’.
d. 2’.

5. What simple safety rule must be followed to make ROPS effective?

a. Wear gloves.
b. Wear hardhat.
c. Wear seatbelt.
d. Wear pantyhose.

6. The type soil most likely to collapse?

a. A.
b. B.
c. C.
d. D.

7. If the excavation is below 5' deep what precaution must be taken before a man can enter the hole?

a. Get a ladder.
b. Get a harness.
c. Get a tape measure.
d. Sloping or engineer approved shoring.

8. In type "C" soil what is the minimum slope required? (Slope to depth)

a. 1:1
b. 1 ½:1
c. 2:1
d. 3:1

9. What should you as an operator do to protect ground personnel?

a. Mark the maximum arc of the bucket.
b. Remove hands and feet from controls before allowing entry into the arc.
c. Have "eye contact" between operator and assistant.
d. Signal the assistant that it is okay to enter the arc.
e. All of the above.

10. According to the COE Safety Concepts what is the minimum safe separation distance that multiple backhoes can operate from each other?

a. 100'.
b. 200'.
c. Same as intrusive team separation.
d. Both b and c are correct.

11. When the backhoe is delivered who is responsible for loading and unloading.

a. Owner.
b. Renter.
c. Government
d. Home Depot

12. Before accepting delivery you should.

a. Check fluids.
b. Operate all controls then check for leaks.
c. Check all safety equipment.
d. Check for proper routing of hoses.
e. All the above.

13. How many people can ride on the backhoe?

_____.

14. How many people can you lift in the front bucket for tree trimming?

_____.

15. What is the minimum distance you can pile your spoil from the edge of the excavation?

a. 1’
b. 2’
c. 3’

d. 4’

OE SECTOR
Standing Operating Procedure (SOP)

MEC Reconnaissance Operations

PARSONS
5390 Triangle Parkway, Suite 100
Norcross, Georgia 30092

Revision No.1
February 2005

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide the minimum procedures and safety and health requirements applicable to the conduct of Munitions and Explosives of Concern (MEC) Reconnaissance (MECR) operations on sites contaminated with unexploded ordnance (UXO).

2.0 SCOPE

This SOP applies to all site personnel involved in MECR operations regardless of affiliation. This SOP is not intended to contain all of the requirements needed to ensure complete compliance, and should be used in conjunction with project plans and applicable Federal, state and local regulations. Consult the documents listed in Section 3.0 of this SOP for additional compliance issues.

3.0 REFERENCES

Applicable sections and paragraphs in the documents listed below will be used as references for the conduct of MECR operations:

- Parsons Corporate Safety and Health Program;
- 29 CFR 1910, OSHA General Industry Standards;
- EP 385-1-95a, CEHNC Basic Safety Concepts and Considerations for OE Operations;
- EM 1110-1-4009, Ordnance and Explosive Response;
- EM 385-1-1, USACE, Safety and Health Requirements Manual; and
- AR 385-10, Army Safety Program

4.0 RESPONSIBILITIES

4.1 UXO Safety Officer

The Parsons UXOSO will implement all safety requirements. He is responsible for safe conduct of operations within all exclusion areas/site work areas and has the authority to halt field operations if a situation warrants it. He provides UXO escort services for all non-UXO personnel and monitors all investigative activity and provides specialist support for identification of MEC.

4.2 UXO Technician III

UXO Technician III supervises the conduct of all onsite activities directly related to MEC operations. He supervises other UXO Technicians in the identification of MEC, including but not limited to fuzes and determining fuze condition. He oversees the operation and maintenance of military and civilian magnetometers and prepares required MECR administrative reports.

4.3 UXO Technician II

UXO Technician II assists in the conduct of all onsite activities related to MEC operations. He is required to identify MEC items, including fuzes and determine fuze condition. He will operate and maintain military and civilian magnetometers, operate navigational/locating equipment and collect required data.

4.4 Other Team Member(s)

UXO Sweep personnel. Sweep personnel assist UXO technicians in the MECR operations only under direct supervision of a qualified UXO technician II or above. This position requires site and job specific training (which will include ordnance recognition, safety precautions, donning and doffing personnel protective equipment, etc.), but does not require UXO technician qualifications. Sweep personnel will conduct visual and/or instrument assisted UXO search activities and perform field maintenance on both military and civilian magnetometers. UXO Sweep personnel are not involved in the excavation of anomalies and are forbidden from handling MEC.

5.0 OPERATIONAL PROCEDURES

5.1 General

All reconnaissance activities involving assessment of possible MEC will be conducted in accordance with the requirements of the U.S. Army Engineering and Support Center, Huntsville, *EP 385-1-95a and EM 1110-1-4009.* Plans shall be based upon the minimum number of personnel, exposed for the minimum amount of time, to the minimum amount of UXO consistent with efficient operations and maximum safety.

5.2 Procedures

To ensure safety of all field personnel, a UXO Technician III will provide a surface sweep and subsurface evaluation using a magnetometer, to provide a cleared route into and out of each area. The UXO Technician(s) will utilize one of the listed pieces of equipment to screen the walking path and sampling locations for surface and shallow buried UXO. Both pieces of equipment are handheld units and are highly sensitive to surface and shallow burial locations of likely UXO.

5.2.1 Types of MECR operations:

5.2.1.1 Type A (Static) Reconnaissance

The site has been surveyed, staked and vegetation removed. Search areas, grids, are laid out in accordance with the site Work Plan (normally 100’ x 100’). The MECR crew starts at the Southwest corner, traveling in an easterly direction, alternating sweep paths from North to South, until the crew has completed the grid at the Southeast corner; while sweeping a 5-foot surface path, with selected magnetometer equipment, and recording all data, as described in the Work Plan.

5.2.1.2 Type B (Meandering Path) Reconnaissance

The site may not have been surveyed, staked or vegetation removed. Search areas, grids, are selected from information collected on previous site visits or from GIS mapping, in accordance with the site Work Plan. The MECR crew will begin sweeping a 5-foot surface path, with selected magnetometer equipment; centered on the southern end of the transect or line; and traveling in a northerly direction, or as described in site specific Work Plan, until the transect or line is completed. Crewmembers must always be in sight of other team members, depending on the vegetation and the predicted past use of the area. Data must be recorded, as described in the Work Plan.

TABLE 5-1 Location Equipment

Equipment Type	Equipment Performance
Schonstedt® GA-52/CX Gradiometers ®	A flux-gate magnetic gradiometers, which detect materials, with ferrous iron content. The GA-52CX uses an audible tone to indicate the intensity of the magnetic signal. The GA-52CX does not digitally record geophysical or global positioning data and are thus called "analog" geophysical instruments. The GA-52CX magnetometers will be used to perform "mag and flag" type surveys in areas that cannot be surveyed using the digital techniques. They will also be used to assist in anomaly reacquisition and analog quality control surveys**.**
Foerster Minex 2FD	A frequency domain electromagnetic analog instrument used for "mag and flag" or "mag and dig" type surveys. The detector utilizes two different operating frequencies simultaneously and is microprocessor controlled in operation for ground exclusion balance, sensitivity adjustment, detection and false alarm signals

Note: Separation distance of 75 feet will be maintained between detection equipment, approaching vehicles and any equipment, which interferes with the instrument

5.2.2 Magnetometer Calibration Point

The MECR team will select an area within the work site that is relatively free of ferrous interference, the placement of a calibration point. Actual size (length and width) of the point will be as long and as wide as necessary to place the calibration anomalies in the ground and not interfere with each other. Those sites that have geophysical prove outs constructed can be used as the magnetometer calibration point.

The calibration anomalies are selected from the Most Probable Munitions (MPM) listing. Inert MEC items, which have been verified, or non-MEC items, of similar size and mass, will be used. The items are buried as stated in the SOW or in a manner illustrated below. The type of ordnance buried is solely dependent upon the MPM and other known ordnance at site.

5.3 Personnel Qualifications:

- Magnetometer operators will be familiar with the operation of the detection equipment.
- UXO personnel are certified by CEHNC-Huntsville
- All Site personnel are OSHA qualified, both 40-hr and current 8-hr Refresher, IAW 29 CFR 1910.120
- All Site personnel operating a vehicle maintain a current state driver's license.

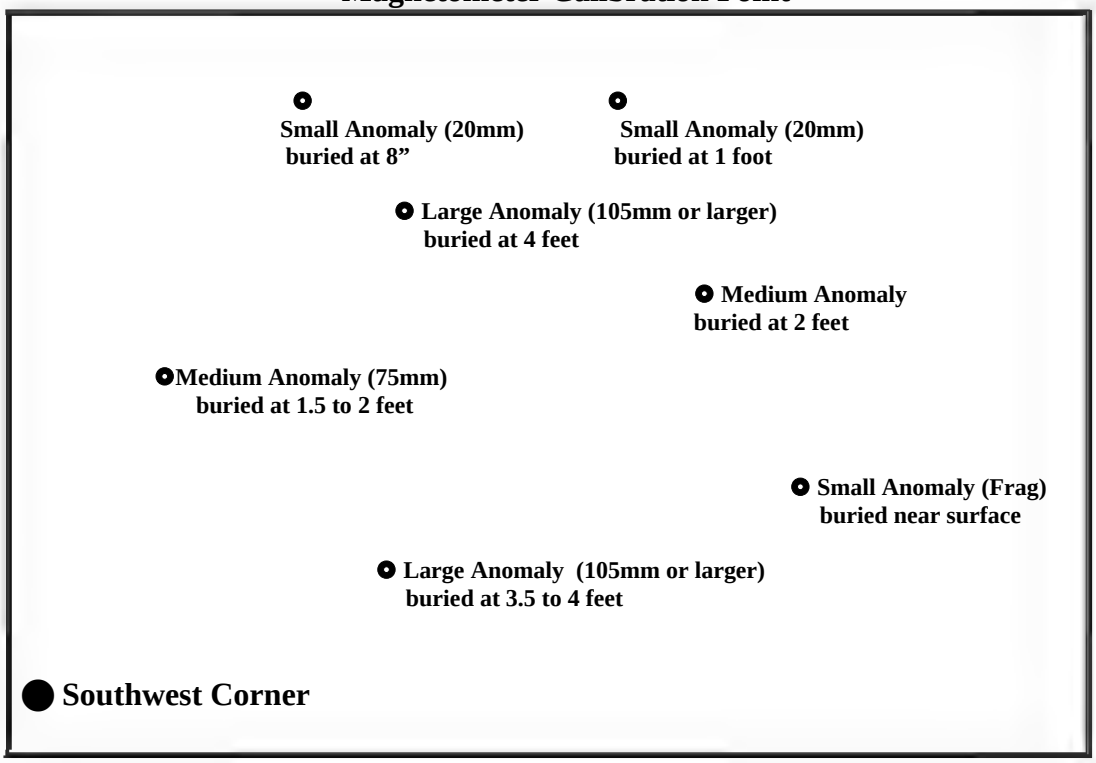
5.4 Calibration of Equipment

5.4.1 Magnetometers: The selected equipment will be calibrated and maintained either daily or IAW manufacturer's suggestion, at the calibration point. The operator will sign the Calibration Log after each calibration. (See Figure 1)

5.4.2 Global Position Systems (GPS): The selected equipment will be calibrated and maintained either daily or IAW manufacturer's suggestion, as described in the Work Plan.

5.4.3 Data Collection System: The selected equipment will be calibrated and maintained either daily or IAW manufacturer's suggestion, as described in the Work Plan.

Table 5-2
Magnetometer Calibration Point



Note: Not to scale. This is an example only

5.5 Site Control

All personnel on-site will follow the guidelines of this SOP.

- Work zones and access points: Site access control will be implemented by the UXOSO and will be accomplished through a program that limits movement and activities of personnel and equipment at the project site.
- Site map delineating work zones: A site map will be used by the UXOSO during the Daily Operational Briefings to inform the workers of the location of hazardous areas on the site, the assembly areas to be used in the event of a site evacuation, and any other information relevant to the day's activities.
- Site security (physical and procedural) description:
- It is anticipated that the site team will be the only personnel on the site.

5.6 Communications

On-site communications will be achieved orally with a contingency for hand signals, and off-site communications will be by cellular phone. All activities will cease, in the event that a field member cannot be accounted for.

6.0 SAFETY PROCEDURES

6.1 General

Using common sense and following safe practices can reduce hazards due to normal site activities. Personnel should keep the guidelines listed below in mind when conducting field activities.

1. Horseplay or fighting is prohibited.
2. Eating, drinking, smoking, chewing gum, tobacco or any other hand-to-face activities are prohibited on the site except in designated areas after face and hands have been washed.
3. When required to sit or kneel on the ground, avoid contaminated surfaces.
4. Placing equipment on contaminated surfaces should be avoided.
5. Climbing on or over obstacles is prohibited. Stacks of materials can be unstable and could cause injury.
6. Open flames of any type are prohibited on site, except in designated areas.
7. Only authorized employees may enter the work site. Visitors must check in with the UXOSO, receive an appropriate safety briefing, and must be escorted by UXO/qualified personnel at all times while on the site.
8. Hazard assessment is a continuous process. Personnel must be aware of their surroundings and constantly be aware of the UXO, chemical and physical hazards that are or may be present.
9. Team members will be familiar with the physical characteristics of each site including wind direction, site access, and the location of communication devices and safety/emergency equipment.
10. Detection or appearance of unusual liquids, odors or discolored soil could indicate the presence of contaminants and should be reported to the UXOSO immediately.
11. Non-UXO qualified personnel will receive site-specific UXO recognition training before participation in site activities.
12. Non-UXO qualified personnel will not touch or disturb any object which could potentially be MEC related, and will immediately notify the nearest UXO qualified person of the presence of the object.
13. Non-UXO qualified personnel will be escorted on site by UXO qualified personnel at all times, until the area is cleared.

6.2 MEC Related Hazards

During all aspects of the MECR operation, site personnel may encounter potential MEC hazards, which are discussed in detail in the Accident Prevention Plan (APP) for the specific project and EP 385-1-95a

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6.3 Biological Hazards

During all aspects of the operation, site personnel may encounter potential biological hazards, which are discussed in detail in the APP.

6.4 Physical Hazards

During all aspects of the operation, site personnel may encounter potential physical hazards, which are discussed detail in the APP.

6.6 Emergency Procedures

A minimum of two (2) personnel who are trained in First Aid and CPR will be onsite at all times that fieldwork is being performed. If an emergency develops on site, the procedures delineated herein and the APP are followed. Emergency conditions exist if:

- Any member of the field crew is involved in an accident or experiences any adverse effects or symptoms of exposure;
- A condition occurs that is more hazardous than anticipated; and/or
- Fires, explosions, structural collapses/failures, and/or unusual weather conditions (thunderstorms, lightning, high winds, etc.) occur.

7.0 PERSONNEL PROTECTIVE EQUIPMENT

7.1 General

Personnel working in close proximity to the established work zones will be required to wear OSHA Level D protection. Level D should be worn only if the activity in which personnel are engaged does not have the potential for splash, immersion or any other contact with hazardous substances. This will consist of at a minimum:

- Work clothes or coveralls (cotton).
- Leather Work gloves.
- Work boots (non-metallic safety toe if foot hazards exists).
- Safety glasses.
- Snake Chaps (if necessary).
- Two-way radio.

Personnel working away from active field investigations will not be required to wear safety glasses or safety boots.

8.0 REPORTS AND LOGS

Site personnel assigned specific tasks will complete required reports and logs, as described in the Work Plan.

STANDARD OPERATING PROCEDURE
FOR
MECHANICAL VEGETATION REMOVAL

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide the minimum procedures and safety and health requirements applicable to the conduct of mechanical vegetation removal operations.

2.0 SCOPE

All personnel performing operations utilizing mechanical equipment for Vegetation Removal shall conform to this SOP. This SOP is not a stand-alone document, and all personnel shall become familiar with associated documents and/or manuals related to this operation.

3.0 REGULATORY REFERENCES

- Parsons Corporate Safety and Health Program
- OSHA General Industry Standards, 29 CFR 1910
- OSHA Construction Standards, 29 CFR 1926
- USACE EM 385-1-1, Safety and Health Requirements Manual
- AR 385-10, Army Safety Program
- Operators Manual and Manufacturers Recommendations

4.0 RESPONSIBILITIES

4.1 Program Manager (PM)

The PM is responsible for ensuring availability of resources required to safely implement this SOP.

4.2 Field Operations Manager (FOM)

The FOM is responsible for incorporating this SOP in plans, procedures, and training.

4.3 UXO Safety Officer (UXOSO)

Ensures that all mechanical vegetation removal operations are being conducted in a safe manner in accordance with the PWP, SSWP, and this SOP.

4.4 Mechanical Vegetation Removal Team Leader

The team leader is responsible for the daily maintenance, upkeep, and repair of the machine and certification of operator personnel.

4.5 UXO Escort/safety Observer

The UXO Escort ensures that personnel and equipment remain within the site, and marks any MEC encountered and reports its location to the OEFOM.

4.6 Team Members

The Team Members are responsible for the proper and safe operation and maintenance of all equipment, such as weed eaters and chainsaws, and walking behind brush hogs and the TAZ.

5.0 MECHANICAL VEGETATION REMOVAL OPERATIONS

Vegetation removal operations shall be consistent with the operators manual and terrain features, and permits the Ground Safety Observer to perform those duties as directed to include a visual search/survey of the area(s) to be worked in.

- Personnel shall not enter within 50 feet of an operating piece of equipment. If, at any time, personnel enter closer than 50 feet, the operator shall immediately stop, return the engine to idle speed, and disengage power to all attachments.

- A communications check with the team personnel prior to operations commencing shall be conducted. Hand signals are devised and used as a secondary means of communication. All team personnel must know these hand signals prior to operations commencing.

- The direction and manner in which the vegetation is to be removed will be directed by the Team Leader. Prior to removal operations commencing, a visual search/survey is conducted to determine the hazards that may be encountered including MEC, terrain slope, vegetation, wildlife, environmental concerns, and PPE requirements.

- The Ground Safety Observer precedes the equipment and performs a visual search for MEC, ordnance scrap, rat's nests, surface debris, and any other obstruction/object that may pose a hazard to team personnel. Hazardous items, impassable terrain, or vegetation that may affect operations will be marked and team personnel notified. The Operator shall follow a route selected by the Ground Safety Observer while operations are ongoing.

- Team personnel ensure that a 6-inch ground clearance is maintained during removal operations. Those areas marked as hazards are to be avoided.

- MEC or MEC-related items encountered are marked and avoided. Notification of these items will be made to the FOM.

5.1 Safety

Safety is paramount. All personnel shall observe those safety precautions/warnings that apply, or may apply, to vegetation removal operations. Those listed below are general in nature and personnel will need to review applicable publications for more specific safety precautions/warnings. Distances are the minimum required.

- Maintain 200 feet from Non-UXO personnel; UXO personnel engaged in intrusive work; and other mechanical equipment (i.e., Backhoe).
- Maintain 50 feet between equipment and team personnel.
- Distances may be increased by the CESPK Safety Specialist or UXOSO, as determined by site history, MEC items encountered, terrain features, and other factors that my apply.
- Use equipment safety features (i.e., guards).
- Safety precautions/warnings found in the operators manual(s)/manufacturer's publication(s) shall be observed.
- Maintain 6 inches of ground clearance during removal operations.
- Communications shall be maintained between the Team Leader/UXO Avoidance Specialist, Operator, and Ground Safety Observer at all times.
- Maintain site control.
- Observe safety precautions for items encountered or suspected.
- Ensure PPE is serviceable and worn/used in a proper manner.
- Mechanical Means Equipment with a greater distance stated will take precedence regarding flying debris.

6.0 PERSONAL PROTECTIVE EQUIPMENT (PPE)

Level D PPE will be required for personnel engaged in mechanical vegetation removal. Clothing includes, but is not limited to:

- Coveralls or work clothing as prescribed;
- Work gloves, leather or canvas as appropriate;
- Safety glasses and face shields when appropriate;
- Hard hats when working within 100 feet of equipment;
- Hearing protection, noise attenuators or ear plugs when within 50 feet of equipment;

- Dust mask, as required by wind conditions and/or the presence of airborne particulate matter; and

- Other PPE as needed (i.e., face shield, Kevlar chaps, etc.)

7.0 TRAINING

All personnel who work on a mechanical vegetation removal crew will be qualified and certified through machine specific, site specific and on-the-job training. This training will consist of:

- Mechanical operations and maintenance of the vegetation removal equipment;

- Features of the equipment and its operational limits and characteristics; and

- Safety parameters relevant to chipping operations.

STANDARD OPERATING PROCEDURE
FOR
MINIATURE OPEN FRONT BARRICADE

1.0 PURPOSE

The Miniature Open Front Barricade (MOFB), also known as the, "Bud Lite" will be employed on the Fort Ord site in areas where nonessential personnel and/or structures are inside the established exclusion zone.

2.0 SCOPE

This scope of work (SOP) applies to all personnel employing the MOFB.

3.0 REGULATORY REFERENCES

- HNC-ED-CS-S-98-8 Miniature Open front Barricade
- CEHNC-OE-CX Interim Guidance Document 00-001 Determination of Appropriate Safety
- Distances on OE Sites
- CEHNC-OE-CX Interim Guidance Document 00-02 Basic Safety Concepts and Considerations For OE Operations
- Parsons Programmatic Work Plan-Fort Ord, California

4.0 RESPONSIBILITIES

4.1 Program Manager (PM)

The PM is responsible for ensuring availability of resources to safely implement this SOP.

4.2 Field Operations Manager (FOM)

The FOM is responsible for incorporating this SOP in plans, procedures and training.

4.3 UXO Safety Officer (UXOSO)

The UXOSO ensures that all operations involving the MOFB are being conducted in a safe manner, in accordance with the PWP, SSWP, and this SOP. The UXOSO will ensure that all personnel are briefed on the hazards associated with the MOFB, and document training of its use.

4.4 UXO Team Supervisor (Technician III)

The Technician III is responsible for the daily maintenance and inspection of the MOFB and ensuring that all team members receive a daily tailgate briefing prior to employing the MOFB. He

will also ensure that all team members are familiar with this SOP and its requirements when employing the MOFB.

5.0 OPERATIONS

- UXO Technicians who employ the MOFB on Fort Ord site will be trained in its use, and thoroughly briefed on the contents of this SOP, and pertinent references.
- The MOFB will be used to investigate suspect ordnance items in areas where establishment of the minimum safe distance (MSD) is not possible, i.e., near the installation boundary or areas in close proximity to occupied structures.
- The MOFB will be erected with the suspect MEC a minimum of six inches inside of the open front. The rear of the MOFB will face the area to be protected.
- All 20 plates will be installed in the MOFB prior to investigation/excavation of the suspect item. The MOFB will be transported to/from the site by trailer or pickup truck. It will be moved between excavation sites by vehicle when terrain and vegetation permits.
- When transporting the MOFB by hand, a minimum of four persons will be used. To minimize weight, the MOFB will be transported with the plates removed.
- The mainframe and plates will be inspected daily prior to use for damage, cracks, dents, bends, etc.
- The largest munition that the MOFB was designed for is the M374 81mm mortar, HE.

6.0 PERSONNEL PROTECTIVE EQUIPMENT

Personnel Protective Equipment (PPE) consisting of level D is required while using the MOFB. PPE requirements will be in accordance with the SSWP requirements when handling and/or excavating MEC.

7.0 GENERAL SAFETY PRECAUTIONS

- All appropriate MEC safety precautions will be observed when employing the MOFB.
- The plates will be installed one at a time.
- The plates will be slowly lowered into the MOFB, not dropped.
- The MOFB will not be used within 200 feet of non-essential personnel or occupied structures.
- Only one person will occupy the MOFB during excavations and investigations.
- Care will be exercised when entering and exiting the MOFB for head clearance.

7.2 Warnings

When installing and removing plates, severe injury to fingers can occur if proper clearance is not maintained.

OE SECTOR
Standing Operating Procedure (SOP)

Severe Weather Operations

PARSONS
5390 Triangle Parkway, Suite 100
Norcross, Georgia 30092

Revision No. 1
February 2005

1.0 PURPOSE

The purpose of this procedure is to provide the minimum requirements and site personnel actions in the event of site evacuation, as a result of severe weather at any Parsons Field operation.

2.0 SCOPE

This SOP applies to all site personnel involved in field operations regardless of affiliation. This SOP is not intended to contain all of the requirements needed to ensure complete compliance, and should be used in conjunction with project plans and applicable Federal, state and local regulations. Consult the documents listed in Section 3.0 of this SOP for additional compliance issues.

3.0 REFERENCES

Applicable sections and paragraphs in the documents listed below will be used as references for the conduct of Severe Weather operations:

- Parsons Corporate Safety and Health Program;
- EP 385-1-95a, CEHNC Basic Safety Concepts and Considerations for OE Operations;
- EM 1110-1-4009, Ordnance and Explosive Response; and
- EM 385-1-1, USACE, Safety and Health Requirements Manual

4.0 RESPONSIBILITIES

4.1 Site Safety and Health Officer (UXOSO)

Upon notification that a severe weather situation exists, the UXOSO will notify site personnel, by radio, cellular phone or sound a horn for 3 five-second blasts. If operations, that might put site personnel at risk, are on going at the time, either the UXOSO or USACE On-Safety Representative will cease all operations and have all teams/crews evacuate to either the site office or the closest “Safe Haven”.

The UXOSO will direct site personnel as to the nature of severe weather and to ready site vehicles for evacuation. During this type of emergency site personnel should not be concerned with assigned vehicles. Time permitting, a select number of site personnel will attempt to safely secure mission essential equipment (e.g. Geophysical GPS/Radio Relay Systems, RTK GPS Systems, computers, etc.) and prepare to evacuate the area to the recommended “Safe Haven”. The UXOSO will maintain radio communications with all site personnel, necessary support elements and record the events in the site Safety Log.

Upon arrival at the “Safe Haven”, the UXOSO will conduct a head count of all site personnel and Site Visitors, using that day’s Daily Safety Brief Sign-In Roster and Site Visitors Log.

4.2 Individual/Personnel initially reporting Severe Weather

The individual or personnel initially spotting a severe weather situation (lightning, tornado) will immediately report it to either the UXOSO or USACE On-Safety Representative by the quickest means possible.

4.3 Site Personnel

Upon the notification to evacuate the work site for the designated Rally Point, site personnel will do so in an orderly manner. Vehicle operators will not exceed the posted or site enforced speed limit, unless directed by USACE On-Site Safety Representative; however that speed will not exceed the conditions of the roadway.

4.4 USACE On-Site Safety Representative

Severe weather occurring before normal working hours, the USACE Site Safety Representative will decide whether a work delay is required and notify the UXOSO. The UXOSO will begin a site recall procedure with all site section supervisors, who will in turn notify their personnel.

5.0 GENERAL INFORMATION

The majority of Parsons field operations are conducted at either heavily wooded sites, or sites that consist of large rolling and sloping pastures and grasslands, consisting of clay or loose sand, and some even contain large areas of ravines and drop-offs. As a result of this, even small amounts of rain could cause vehicle entry/exit problems and personnel slipping hazards that may result in damage or injury to site personnel and equipment.

Almost all of the areas are susceptible to severe thunderstorms, with heavy downpours of rain, lightning, hail, strong microburst winds, flash floods and tornadoes. These storms are known to manifest themselves very quickly and leave very little time to react. In the event of severe weather in the area, the UXOSO maintains a portable Severe Weather Alert radio and the Site Manager will have access to the National Weather Advisory system, via the internet or by phone.

5.1 Thunderstorms

Thunderstorms affect relatively small areas when compared with hurricanes and winter storms. Despite their small size, ALL thunderstorms are dangerous. The typical thunderstorm is 1.5 miles in diameter and lasts an average of 30 minutes. In order for a thunderstorm to form it needs three things; Moisture – to form clouds and rain; Unstable Air – warm air that can rise rapidly; and Lift – cold or warm fronts, sea breezes, mountains, or the sun's heat are capable of lifting air to help form thunderstorms.

The life cycle of a thunderstorm constitutes three distinct stages, which are detailed below:

- Developing Stage – Towering cumulus cloud indicates rising air; little if any rain during this stage; and occasional lightning.
- Mature Stage – Most likely time for hail, heavy rain, frequent lightning, strong winds, and tornadoes; storm occasionally has a black or dark green appearance; and lasts an average of 10 – 20 minutes but may last much longer in some cases.

- Dissipating Stage – Rainfall decreases in intensity; can still produce a burst of strong winds; and lightning remains a danger.

5.1.1 How Far Away is the Thunderstorm?

- Count the number of seconds between a flash of lightning and the next clap of thunder.
- Divide the number of seconds by five (5) to determine the distance to the lightning in miles.

5.2 Lightning

Lightning poses the greatest potential threat to site personnel and site operations, due to its unpredictable nature. Lightning results from the buildup and discharge of electrical energy between positively and negatively charged areas. Rising and descending air within a thunderstorm separates these positive and negative charges. Water and ice particles also effect distribution.

A cloud-to-ground lightning strike begins as an invisible channel of electrically charged air moving from the cloud toward the ground. When one channel nears an object on the ground, a powerful surge of electricity from the ground moves upward to the clouds and produces the visible lightning strike.

In accordance with current USACE policies, all operations cease when lightning is observed and the "Flash to Bang Time" is 30 seconds or less (approx 6 miles from site). The safe evacuation of personnel is paramount and equipment is secondary.

Those site personnel in and around the site office will seek shelter inside the building. Site personnel working out in the field will seek shelter inside a site vehicle with the windows rolled up and the doors closed.

Site personnel that are using any electronic equipment with an antenna (i.e. RTK system, G-858 or EM-61, etc.) will cease all operations and seek shelter upon visually seeing lightning at any distance.

5.2.1 30/30 Lightning Safety Rule

Go indoors or seek shelter if, after seeing lightning, you cannot count to 30 before hearing thunder. Stay indoors or under shelter for 30 minutes after hearing the last clap of thunder.

5.2.2 Lightning Safety Rules

- Move to a sturdy building or car. Do not take shelter in small sheds, under isolated trees, or in convertible automobiles. Stay away from tall objects such as towers, fences, telephone poles, and power lines.
- If lightning is occurring and a sturdy shelter is not available, get inside a hard top automobile and keep the windows up. Avoid touching any metal.
- Utility lines and metal pipes can conduct electricity. Unplug appliances, office machines etc. not necessary for obtaining weather information. Avoid using the telephone or any electrical item. Use phones **ONLY** in an emergency.

5.2.3 If Caught Outdoors and No Shelter is Available

- Find a low spot away from trees, fences, and poles. Make sure the place you pick is not subject to flooding.
- If you are in the woods, take shelter under the shorter trees.
- If you feel your skin tingle or your hair stand on end, squat low to the ground on the balls of your feet. Place your hands over your ears and your head between your legs. Make yourself the smallest target possible and minimize your contact with the ground. **DO NOT** lay down.

5.3 Tornadoes

Tornadoes produce extreme high destructive winds and devastation. Tornadoes are generally produced along the leading edges of thunderstorms that form, with little or no warning. Before thunderstorms develop, a change in wind direction and an increase in wind speed with increasing height create an invisible, horizontal spinning effect in the lower atmosphere. Rising air within the thunderstorm updraft tilts the rotating air from horizontal to vertical. An area of rotation, 2 – 6 miles wide, now extends through much of the storm. Most tornadoes form within this area of strong rotation.

Most project sites do not afford adequate tornado "Safe Havens", or adequate "Safe Havens" are so far away that they afford little or no help to those site personnel working in remote site locations (Remote Operations are discussed further in this SOP).

The UXOSO and Site Manager will attempt to locate those "Safe Havens" and brief site personnel of their locations, during the Daily Tailgate Safety Briefing.

5.3.1 When and Where Tornadoes Occur

- Tornadoes can occur any time of the year.
- Tornadoes have occurred in every state, but they are most frequent east of the Rocky Mountains during the spring and summer months.
- In the southern states, peak tornado occurrence is March – May, while peak months in the northern states are during the late spring and summer.
- Tornadoes are most likely to occur between 3 and 9 p.m., but can occur anytime.
- The average tornado moves from southwest to northeast.
- Tornadoes can accompany tropical storms and hurricanes as they move onto land.

5.3.2 Tornado Safety Rules

- In a building, move to a pre-designated shelter, such as a basement.
- If a below ground shelter is not available, move to a small interior room or hallway on the lowest floor and get under a sturdy piece of furniture. Put as many walls as possible between you and the outside.

- Stay away from windows.
- Get out of automobiles.
- Do not try to outrun a tornado in your car; instead, leave it immediately for safe shelter.
- If caught outside or in a vehicle, lie flat in a nearby ditch or depression and cover your head with your hands.
- Be aware of flying debris. Flying debris from tornadoes causes most fatalities and injuries.
- Office trailers, even if tied down, offer little protection from tornadoes. You should leave an office trailer and go to the lowest floor of a sturdy nearby building, or follow the procedures detailed in the 6th bullet above.

5.4 Flash Floods/Floods

Due to the massive amounts of rain that can be dropped from thunderstorms the site may be susceptible to flash floods. Some of the existing roads may be unimproved dirt and are easily turned into mud, creating an unsafe driving environment. Those roadways that are paved also place the vehicle in low-lying areas that may be washed out. Do not attempt to cross any roadway that has become submerged by water.

5.4.1 Flash Flood/Flood Safety Rules

- If you are in a low lying area, at the first sign of rain evacuate to high ground.
- Designate an evacuation route in the event of flooding.
- Avoid walking or driving in flood waters.
- Stay away from high water, storm drains, ditches, ravines, or culverts. If the water is moving swiftly, even water only six (6) inches deep can knock you off your feet.
- If you come upon flood waters, stop, turn around, and go another way.

5.5 Straight-line/High Winds

When this is associated with a passing front generating potential severe weather, the winds can increase in speed rather rapidly. Dust and debris pose an eye hazard. High winds can rip vehicle doors and rear hatches from site personnel's grasp causing damage and injury. Site personnel in the field should select an area or park the vehicle in such a matter that provides a windbreak. If this can not be accomplished, open doors and hatches with care. Vehicles should not be left with doors, hoods or hatches open.

5.5.1 Straight-line/High Winds Safety Rules

- In a building, move to a pre-designated shelter, such as a basement.

- If a below ground shelter is not available, move to a small interior room or hallway on the lowest floor and get under a sturdy piece of furniture. Put as many walls as possible between you and the outside.

- Stay away from windows.

- If caught outside, lie flat in a nearby ditch or depression and cover your head with your hands.

- Be aware of flying debris. Flying debris from tornadoes causes most fatalities and injuries.

- Office trailers, even if tied down, offer little protection from straight-line/high winds. You should leave an office trailer and go to the lowest floor of a sturdy nearby building, or follow the procedures detailed in the 4th bullet above.

- Move to a sturdy building or car. Do not take shelter in small sheds, under isolated trees, or in convertible automobiles.

- If high winds are occurring and a sturdy shelter is not available, get inside a hard top automobile and keep the windows up.

5.6 Hail

Hail can occur in conjunction with a thunderstorm and can cause damage to equipment and injuries to personnel. Hail occurs when strong rising currents of air within a storm, called updrafts, carry water droplets to a height where freezing occurs. These water droplets become frozen and the ice particles grow in size, becoming too heavy to be supported by the updraft, and fall to the ground. Speeds of the falling ice particles, hail, can exceed 100 miles an hour, with size exceeding that of a softball.

5.6.1 Hail safety Rules

- Seek shelter, preferably in a building, or hard-top automobile.

- If in the open seek shelter in a culvert if there is no flooding under a rock outcrop or under trees if there is no lightning associated with the hail storm.

- Exercise caution when driving on hail, it is very slippery, so avoid it if at all possible.

- If driving when a hail storm starts pull under an overpass if possible, if not pull well off the road with your lights on in order that advancing motorists can see you.

STANDARD OPERATING PROCEDURE
FOR
UXO TECHNICIANS ANALOG LOCATOR QC QUALIFICATION

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to qualify UXO Technicians utilizing the hand held analog flux gate magnetic locator equipment at the QC qualification grids.

2.0 PROCESS SUMMARY

Qualification and training will be conducted in the designated Badger Flats grids and is not to exceed a total of 90 minutes. The QC training grids will consist of established lanes in the "known" seeded grids that were utilized for the ODDS study and contain sub-surface inert MEC items and/or MEC fragments. The QC qualification grids will consist of established lanes in the "unknown" seeded grids that were also utilized for the ODDS study and contain sub-surface inert MEC items and/or MEC fragments. The UXOQC representative will brief the lesson plan on the analog locator that is used on the project site to conduct analog removal to depth. Following the briefing all UXO Technicians will be provided the opportunity to practice their skills in the training lanes prior to challenging the qualification test. The UXO Technician must locate all items, a minimum of four in each test lane, to successfully attain the UXOQC qualification. All qualification results will be recorded by UXOQC and the documented in of each UXO Technician's training file.

3.0 RESPONSIBILITES

3.1 Program Manager (PM)

The PM is responsible for ensuring availability of resources to safely and effectively implement this SOP.

3.2 Field Operations Manager (FOM)

The FOM is responsible for incorporating this SOP in plans, procedures and training, and ensuring compliance during field operations.

3.3 UXO Safety Officer (UXOSO)

The UXOSO ensures that all mechanical sifting operations are conducted in a safe manner, in accordance with the PWP, SSWP, this SOP, and all applicable regulatory guidance.

3.4 Quality Control Manager (QCM)

The QCM is responsible for ensuring this SOP is effectively implemented.

3.5 UXO QC Personnel (UXOQC)

A UXOQC personnel will ensure that the qualification grid is configured IAW this SOP for a UXO Technicians test and evaluate and instruct the field analog locator process.

4.0 PROCEDURES

The following procedures should be followed to conduct the qualification of UXO Technicians:

Pre- Qualification Training

- UXOQC personnel will conduct a briefing to include the Schonstedt lesson plan developed for all UXO personnel. Additionally, the training and test boundaries with criteria requirements for a successful sub-surface sweep qualification will be identified.

- UXOQC personnel will confirm that all UXO personnel have conducted the equipment checkout procedure required as applicable prior to commencing their individual training.

- Conduct UXO Technician locator training. Training will be carried out in the designated training grids. These grids will have 3' x 100' lanes identified with lane tape. Each lane will contain known depths and locations of MEC and/or MEC fragment to assist the UXO Technician in establishing a baseline for the audible tones that the locator produces. This phase of the qualification process is not to exceed 60 minutes.

- UXOQC personnel will evaluate the effectiveness of the UXO Technician's sweep procedure. Observe that locator sweeps are conducted correctly, side to side, that the instrument search sensor is kept parallel and close to the ground throughout the side-to-side sweeping motion, and that the magnetic locator is operated in accordance with EMR protocol. All observations will be discussed with the individual UXO Technician.

Qualification Test

- There are a minimum of 4 seeded items per established test lane (3' x 50') in the UXOQC Qualification Grids within contract criteria parameters. All sub-surface items are required to be located within a radial error of 18" to pass the qualification process. The UXO Technician challenging the qualification grid lane is to place a flag in the location that he/she determines an item requiring investigation is. UXOQC personnel will validate the flag positions with a GPS unit.

- If any seeded items are missed the UXO Technician will be given an opportunity for an immediate re-test using a different magnetic locator. The use of a different locator reduces the possibility of the individual's test to be unsuccessful as a result of an unserviceable locating instrument. If the retest is unsuccessful all pertinent information and any additional training requirements and/or recommendations to assist individuals in preparation for their retest will be forwarded to the SUXOS for review. The unsuccessful candidate must receive additional training prior to any UXOQC re-testing. Re-testing and corrective action is to be accomplished within eight work days unless the SUXOS has identified extenuating circumstances which require additional time and communicates these to the QCM for an extension approval.

Activity Completion

- Submit a copy of the completed personnel qualification log to the SUXOS for each individual who challenged the qualification test. The original personnel qualification log will be maintained by the UXOSO personnel training files and a copy will be maintained in the UXOQC Office files. Ensure that any unsuccessful personnel report to the SUXOS prior to joining his/her team in the field for additional direction.

Special Requirements

- Previously qualified UXO Technicians who have a break of 90 consecutive workdays will be re-qualified upon there return prior to conducting removal to depth excavations.

- UXO Technicians identified by the SUXOS, UXO Supervisor, and/or during a UXOQC surveillance audit as requiring additional training will be re-qualified.

5.0 UXO Hand-held Analog Magnetic Locator QC Qualification Log

The following log will be utilized to record all personnel qualifications conducted and serve as a record of the individual's analog locator qualification history.

Name:	**Member ID:**	**Team #:**	**Date:**

Analog Locator Unit Serial Numbers:

1.

2.

Item No.	Was Target Found?		Location of Target Report		Radial Error of Target Location (inches)	Comments
	YES	NO	GPS Easting (ft)	GPS Northing (ft)		

UXOQC Name:	**Signature:**	**Date:**

OE SECTOR
Standing Operating Procedure (SOP)

Vehicle Operations

PARSONS
5390 Triangle Parkway, Suite 100
Norcross, Georgia 30092

Revision No. 2
February 2005

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide the minimum safety and health requirements and procedures applicable to the operations involving the use of on and off-road motor vehicles.

2.0 SCOPE

This SOP applies to all site personnel, to include contractor and subcontractor personnel, involved in the conduct of operations involving motor vehicles. This SOP is not intended to contain all requirements to ensure regulatory compliance. Consult documents listed in Section 3.0 of this SOP for additional compliance issues.

3.0 REGULATORY REFERENCES

The following Occupational Safety and Health Administration (OSHA) standards and U.S. Army Corps of Engineers (USACE) requirements directly apply to vehicle operations. References used in preparation of the document are listed below:

- Applicable sections of OSHA Construction Industry Standard 29 CFR, Part 1926.601;
- Applicable sections of Department of Transportation 49 CFR, Parts 100-199; and 571
- USCAE Engineer Manual (EM) 385-1-1, Section 18.

4.0 RESPONSIBILITIES

4.1 Project Manager

The Project Manager (PM) will be responsible for ensuring the availability of the resources needed to implement this SOP, and shall also ensure that this SOP is incorporated into plans, procedures, and training for sites where vehicular equipment is to be used.

4.2 Site Manager

The Site Manager (SM) will ensure that this SOP is implemented for motor vehicle operations. The SM will also ensure that relevant sections of this SOP are discussed in the tailgate safety briefings, and that information related to its daily implementation is documented in the Site Operations Log.

4.3 UXO Safety Officer

The UXO Safety Officer (UXOSO) will be responsible for ensuring that the safety hazards and mitigation techniques associated with this SOP are discussed during the initial Site Specific Safety Training. The UXOSO will also be responsible for daily inspection of site operations and conditions to ensure their initial, and continued, compliance with this SOP and other regulatory guidelines. The UXOSO will also compile a monthly total of mileage or hours of usage of all site vehicles, post those totals predominately in the Site Field Office and report them to the Parsons OE Sector Administrative Assistant (See Figure 1).

4.4 Vehicle Operators

All personnel operating a vehicular piece of equipment will posses a valid drivers license, proof of proficiency on the item in question, i.e., certificate of training, and strictly adhere to the procedures stipulated in this SOP.

5.0 PROCEDURES

All personnel, including contractor and subcontractor personnel, involved in motor vehicle operations shall be familiar with the potential safety hazards associated with the operation of vehicular equipment, and with the work practices and mitigation techniques to be used to reduce or eliminate these hazards.

5.1 General Requirements

Motor Vehicle shall mean any vehicle propelled by a self-contained power unit, or equipment designed for use on paved roads. **All-purpose utility vehicle (APUV)** shall mean any four-wheeled or greater, vehicle propelled by a self-contained power unit, designed for off-road use, such as a Gator, or MULE. From this point forward the term vehicle shall constitute both motor vehicle and APU vehicles unless otherwise stated. Every individual operating a vehicle shall possess a permit (as required by state or federal law) valid for the equipment being operated. No vehicle shall be placed in service until it has been inspected and found to be in a safe operating condition (See Figure 2).

All vehicles shall be inspected and maintained IAW the manufactures recommendations and this SOP. Vehicles being used shall be checked at the beginning of each day to ensure that all parts, equipment, and accessories are in safe operating condition and free of apparent damage that could cause failure while in use. The parts, equipment, and accessories of concern include service brakes, including trailer brake connections; parking system (hand brake); emergency-stopping system (brakes); tires; horn; steering mechanism; coupling devices; seat belts and lap-shoulder restraints; operating controls; and safety devices. These requirements also apply to equipment such as lights, reflectors; windshield wipers, defrosters, fire extinguishers and first aid kits, where such equipment is required. Vehicles not meeting safe operating conditions shall be removed from service, repaired or replaced, and re-inspected prior to being placed back in service.

All vehicles operated between sunset and sunrise shall have the following:

- Two headlights, one on each side;
- Directional signal lights, both front rear;
- Rear Brake Lights, one on each side, and
- Rear Back-up Lights, one on each side

All vehicles, except APUV's, trailers or semi-trailers, having a gross weight of 5,000 pounds or less, shall be equipped with service brakes and manually-operated parking brakes. Service and parking brakes shall be adequate to control the movement of, to stop, and to hold the vehicle under all conditions of service. Service brakes on trailers and semi-trailers shall be controlled from the driver's seat of the prime mover.

Braking systems on every vehicle shall be designed as to be in approximate synchronization on all wheels and develop the required braking effort on the rearmost wheels first, unless the vehicle is equipped with an "Anti-lock Braking System" (ABS). The design shall also provide for application of the brakes by the driver of the prime mover. Exceptions to this are vehicles in tow by an approved tow bar hitch.

Every motor vehicle shall be equipped with the following:

- A working speedometer
- A fuel gauge
- An audible warning device (horn)
- A windshield equipped with an adequate powered windshield wiper
- An operable defrosting and defogging system
- Adequate rear view mirror, or mirrors
- Cabs, cab shields, and other protection to protect the driver from hazards of falling or shifting materials/loads
- Non-slip surfaces on steps
- Safety glass in windshields, windows, and doors
- No cracked or broken glass
- All towing devices that are structurally adequate for the weight drawn, and properly mounted
- A power-operated starting device
- One fire extinguisher, rated at 5 BC units (project provided)
- One First Aid Kit and other appropriate first aid equipment (project provided)

All trailers will be equipped as follows:

- A locking device, or double safety system, shall be provided on every fifth wheel mechanism and tow bar arrangement, which will prevent the accidental separation of towed and towing vehicles;
- Every trailer shall be coupled with safety chains or cables to the towing vehicle. Such chain or cable shall prevent the separation of the vehicles in the event of failure of the tow bar;
- While unhooked from the towing vehicle, all trailers shall be equipped with the approved and adequate wheel chocks to prevent roll-back; and
- A manufacturer's attached support leg system at or near the tongue of the trailer to prevent trailer collapse. In event the trailer is not equipped with a support leg system; the use of intact "cinder blocks" may be used. **Note:** Once the "cinder blocks" are observed with cracks or become broken, they will be replaced and not used again as a support leg.

All buses, trucks, and combination of vehicles with a carrying capacity of 12 tons or greater, when operated on public highways, shall be equipped with emergency equipment required by state laws but not less than those listed below:

- One red flag, not less than 12 inches square, and 3 reflective markers, which shall be available for immediate use, in case of emergency stops;

- Two approved wheel chocks for each vehicle, or each unit of a combination of vehicles;
- One fire extinguisher rated at 20 BC units or two 10 BC rated units, being required for flammable cargoes, including explosives and Munitions and Explosives of Concern (MEC);
- Vehicle exhaust control, so as to present no hazard to the operator, passengers, or other personnel; and
- All rubber-tired motor vehicles should be equipped with fenders. However mud flaps may be used in lieu of fenders, whenever motor vehicle equipment is not designed for fenders.

5.2 Safe Operating Rules

No vehicle shall be driven at a speed greater than the posted speed limit, with due regard for weather, traffic, intersections, width, and character of the roadway, type of vehicle, and any other existing conditions. The operator must, at all times, and under all conditions, have the vehicle under such control as to be able to bring it to a complete stop within the clear distance ahead. To accomplish this, the operator shall follow the safe operating rules presented below:

- No vehicle shall be driven on a downgrade with gears in neutral or with clutch disengaged;
- Every vehicle, upon approaching an unguarded railroad crossing or drawbridge, shall sloe down to a speed as to permit stopping before reaching the nearest track or the edge of the bridge, and shall proceed only if the course is clear;
- No vehicle shall be stopped, parked, or left standing on any road, or adjacent thereto, or in any area in such a manner, as to endanger the vehicle, other vehicles, equipment, or personnel using or passing that area;
- No vehicle shall be left unattended until the motor has been shut off, the key removed (unless the WP directs otherwise), the parking brake set, and the gear engaged in park (automatic) or placed in neutral (manual);
- If stopped on a hill or grade, front wheels shall be turned or hooked into the curb or the wheels securely chocked;
- Personnel shall not be permitted to get between a towed and towing vehicle, until the towing vehicle has been placed in park, parking brake set, and engine turned off;
- When backing or maneuvering buses, trucks, or truck/trailer combination not equipped with an audible backing warning device, the operator will use a ground guide. All other vehicle types, when backing or maneuvering, will check the area and sound their horn;
- Operators of vehicles transporting personnel, explosives, or flammable or toxic substances shall stop at railroad crossings or drawbridges, and shall not proceed until the route is determined to be clear. A stop shall be required at a crossing within a business or residential district that is protected by a watch person, traffic officer, or by a traffic signal giving positive indication to approaching vehicles;
- When a bus, truck, or truck/trailer combination is disabled or parked on the traveled portion of a highway or the shoulder adjacent thereto, red flags shall be displayed during the daytime and reflector, flares, or electric lights at night (An exception may be made in residential or business sections or municipalities);
- The principles of defensive driving shall be practiced at all times;

- Seat belts and lap-shoulder restraints will be installed and worn IAW 49 CFR 571 (DOT);
- If the windshield wipers are in use due to rain, headlights will be activated; and
- During high winds, extreme care is required when opening vehicle doors, hoods and hatches. High winds can rip vehicle doors and rear hatches from a persons grasp causing damage and injury. Site personnel should select an area or park the vehicle in such a manner that provides a windbreak. Vehicles should not be left with doors, hoods or hatches open.

5.3 Transportation of Personnel

The number of passengers in passenger-type vehicles shall not exceed the number of seats with approved seat belts. Trucks used to transport personnel shall be equipped with a seating arrangement that is securely anchored, a rear gate, a guardrail, and steps or ladders for mounting and dismounting. The beds of trucks which are not equipped with the appropriate safety devices, as described in this paragraph, will not be used to transport personnel unless absolutely necessary, and never on a public highway, unless it is an emergency. Additional personnel transportation requirements are listed below:

- All tools and equipment shall be guarded, stowed, and secured when transported with personnel;
- No person will be permitted to ride with arms or legs outside of the truck's body, in a standing position on the body, on running boards, or seated on side fenders, cabs, cab shields, rear of truck, or on the cargo load;
- All motor vehicles transporting personnel during cold or inclement weather shall be enclosed;
- No explosives, flammable materials (except normal fuel supply), or toxic substances shall be transported in the cabs of any vehicle or beds of vehicles being used to transport personnel;
- No vehicle transporting personnel shall be moved until the driver has ascertained that all individuals are seated, belted, the guardrail and rear gate are in place, and doors are closed; and
- Getting on or off any vehicle while in motion is prohibited.

5.4 Fueling

All vehicles shall be shut off during fueling operations, operators and passengers will refrain from using cellular telephones, and no smoking or open flames will be permitted within 50 feet of fueling operations. Care should be taken not to spill fuel, and only that fuel recommended by the vehicle manufacturer shall be used. When fueling from a portable fuel tank system, the vehicle and portable tank will be bonded to each other (Example of this – using "jumper" cables to connect the tank and vehicle). During fueling, when there is a potential for fuel contact with the skin, especially during cold weather, personnel will wear protective gloves, as specified in the SSHP.

5.5 Loading

Drivers of trucks and similar vehicles shall leave the cab, if the cab of the vehicle being loaded is exposed to danger from suspended or overhead loading operations, unless the cab is adequately protected. No motor vehicle shall be loaded so as to obscure the driver's view ahead or to either side, or to interfere with the safe operation of such vehicle. All vehicles carrying

loads which project more than 4 feet beyond the rear of the vehicle shall carry a red light at or near the end of the projection at night, or when atmospheric conditions restrict visibility. During daylight periods, or other non-restricted conditions, a red flag not less than 12 inches square shall be used. The load shall be distributed, checked, tied down, or secured.

5.6 All-Terrain Vehicles

During the operation of all-purpose utility vehicles (APUV's), every operator shall possess a valid state driver's license and have completed, as a minimum, an approved on-site APUV training course prior to operation of the vehicle. See USACE EM 385-1-1, Section 18D for additional information. The operation of APUV's shall be conducted according to the procedures listed below:

- The manufacturer's recommended payload shall not be exceeded at any time;
- Gloves and an approved motorcycle helmet with face shield or goggles shall be worn at all times while operating an APUV;
- APUV's are to be used on off-road terrain and gravel and dirt roads, never on a public road;
- APUV's shall be driven during daylight hours only;
- Only four-wheel, or greater, APUV's shall be used;
- Passengers are prohibited on APUV's, unless they are designed to accommodate additional passengers, i.e., additional seats, and any passenger shall be required to wear a motorcycle helmet with fact shield or goggles; and
- All APUV's shall be equipped with warning signal devices and a horn.

5.7 Maintenance

All vehicles will be maintained IAW the manufacturer's requirements and guidelines. All vehicles will be inspected prior to operation and on a weekly basis for safety and basic operational equipment for deficiencies and parts needing repair. These will be brought to the attention of both the operator's supervisor and the UXOSO. Vehicles requiring repair or manufacturers required maintenance (except of oil changes, lubrication or tire rotation) will be repaired and dead-lined until the repairs are made.

All vehicles will be cleaned weekly and trash will be removed on a daily basis from inside the cab and truck bed. Excessive trash inside the operator's or passenger's compartment is unsafe and a health hazard for others. Excessive build up of mud inside the motor vehicle's wheel wells preclude the operator to observe any vehicle deficiencies and cause unsafe vehicle operations. All motor vehicles at Parsons sites will display a clean and up-kept appearance at all times, regardless of the site's operation, unless otherwise directed by local water restrictions.

5.8 Log Books and Operating Manuals

All motor vehicles will have their Operating Manuals and Log Books, for those vehicles, with the vehicle at all times. The log book will be up-to-date and complete.

ATTACHMENTS

- Figure 1 – Parsons Form D0038.xls (Monthly Mileage Report)
- Figure 2 – Parsons Form (Weekly Vehicle Inspection)
- Figure 3 – Parsons Activity Hazard Analysis (All-Terrain Vehicles)

Accident Exposure Data Report

Parsons
Contract Number: DACA87-00-D0038
Date:

Task Order #	Name	Location	Total of Field Hours Expended *	Vehicle Miles	Lost Work Days for the Month **	Total Lost Work Days	Number of Vehicle Accidents

This is a sample format; actual form is an Excel Spreadsheet. Do not use this form
* - Including Subcontractors (list each one separately)
** - Due to On-the-Job Accidents

Ed Grunwald, Corporate Health and Safety Officer

Figure 1

Weekly Vehicle Inspection Report

Date:	**Vehicle Make:**	**Rental/Lease/Private** *(circle one)*
Lic Plate #:	**Veh VIN#:**	
Starting Mileage for Week:	**Ending Mileage for Week:**	
General Vehicle Inspection		

Check { } with R for repair needed; X for OK; / for adjustment made

1. Windshield { }	**3. Vehicle Interior { }**
2. Vehicle Exterior { }	**4. Leaks { }**

5. Lights:

a. Headlights	**{ }**	d. Brake Lights	**{ }**
b. Tail lights	**{ }**	e. Back-up Lights	**{ }**
c. Turn Signals	**{ }**	f. Interior Lights	**{ }**

6. Brakes { }	**10. Belts { }**
7. Horn { }	**11. Defroster { }**
8. Tires (Tread wear/pressure) **{ }**	**12.Radiator/Hoses** (DON'T check when hot) **{ }**
9. Windshield Wipers/Washer { }	**13. Battery { }**

14. Fluid Levels: (Circle approximate level)

a. Oil	Full	1qt low		Added
b. Coolant:	Full	Need coolant		Added
c. Transmission:	Full	1pt low		Added
d. Fuel:	Full	½	¼	Empty

Comments/Repairs/Service(s) Needed:

Figure 2

Certification of Task Hazard Assessment

TASK NAME: ALL TERRAIN VEHICLE (ATV)

1.0 PRINCIPAL TASK STEPS		
Principal Steps: 1. Accepted/Inspected at Site 2. Placed in Operation 3. Vehicle Maintenance	**Potential Site Hazards** (See 1.1 list): Vehicle Safety A1-2, B1-3, C, D1-2, F, H2-4, J1, K1-3 Vehicle Safety	**Recommended Controls** (See 1.2 list): A through D A through O A through D

1.1 Potential Hazards: Items checked are known or anticipated site hazards, or may occur as a result of site operations **(Check Appropriate Box)**

A ( ) Thermal Stress A1( ) Heat Stress A2( ) Cold Stress B( ) Biological Hazards B1( ) Toxic/Hazardous plants B2( ) Hazardous animals/insects B3( ) Hanta Virus, when present C( ) Vehicle traffic in work area(s) D( ) Fire Hazards D1( ) Vegetation (high grass areas) D2( ) Flammable Liquids	E( ) Manual Lifting Hazards F( ) Slip, trip or fall G( ) Chemical Hazards G1( ) Respiratory G2( ) Skin H( ) Vehicle Operations H1( ) High Noise (>85 dBA) H2( ) Overhead Hazards H3( ) Pinch Points Hazards H4( ) Hot Surfaces	J( ) Radiation J1( ) UV J2( ) Ionizing K( ) MEC Environment K1( ) Potential MEC items K2( ) Unplanned Detonation K3( ) Near Surface

1.2 Recommended Controls:

A. Observe all MEC safety precautions and use safe work practices, IAW EP 385-1-95a, Basic Safety Concepts for O&E Operations, Jun01 and EM 385-1-1, Safety and Health Requirements Manual.
B. All ATV Equipment will be inspected and tested, in accordance with manufacturer's recommendations and certified in writing by a component person prior to being placed in use, IAW Section 18, EM 385-1-1.
C. All ATV operators will be licensed and trained by a recognized accredited ATV Training Course or in-house resource that is certified as a Trainer by an accredited organization, prior to operations of the vehicle.
D. Wear the appropriate PPE for the task being performed.
E. Use recognized hand and arm signals to communicate between the operators. Cease any operation, when this fails.
F. Maintain safe and appropriate separation distances between ATV, when traveling as a group.
G. ATVs will be used only off road, unless equipped for paved road use by manufacturer.
H. ATVs will only be operated during daylight hours, unless equipped for night use by manufacturer.
I. Only ATVs with four or more wheels may be used.
J. The manufacturer's recommended payload will not be exceeded at any time.
K. Passengers are prohibited on Class I ATVs (Class I ATV – single seat centered over the engine).
L. All ATVs will be equipped with mufflers, spark arrester, tail lights, stop lights and an audible signal device (horn).
M. Use of "ground guides" will be used, when vehicle(s) are not equipped with an audible warning device and/or has an obstructed view. When transporting equipment by trailers, the trailer will be "chocked" with approved devices when unhooked from the transporting vehicle. When attempting to hook onto the trailer, "ground guides" will not place any part of between the trailer and vehicle.
N. Be alert. Mark, avoid, and report any suspect MEC items.
O. Do not handle wildlife. Review characteristics of potential toxic/poisonous plant life known in the area.

2.0 DEGREE OF OVERALL TASK HAZARD: Anticipated degree of hazard, based on the hazards associated with this task.

Chemical Hazard:	**Physical Hazard:**	**Biological Hazard:**
( ) Low ( ) Serious ( ) Moderate ( ) Unknown	( ) Low ( ) Serious ( ) Moderate ( ) Unknown	( ) Low ( ) Serious ( ) Moderate ( ) Unknown

3.0 PROTECTIVE MEASURES: Items checked will be used to control or mitigate the above mentioned hazards

( ) Tailgate Safety Briefing ( ) Specialized Training ( ) Proper operations of equipment ( ) Equipment Safety hazards ( ) Personal protective equipment Other: _____	( ) Engineering Controls ( ) Lockout/Tag Out ( ) Site Control Zones ( ) Communications ( ) Establishing Safe Work Areas ( ) Designate Smoking/Break Area ( ) Proper use of vehicles ( ) Proper use of seat belts Other: _____	( ) Administrative Controls ( ) Rotate Workers ( ) Limit Exposure Time ( ) Decontamination **( )** Wash Hands at break regardless of activity Other: _____

TASK NAME: ALL TERRAIN VEHICLE (ATV)

4.0 Applicable SOPs/Programs: Site Specific Safety/ Health Plan (SSHP)

5.0 PPE: PPE has been assigned based on the potential for exposure as identified by this hazard assessment

Level of Protection	( ) A ( ) B	( ) C ( ) D	( ) Modified
Respiratory Protection	( ) SCBA ( ) Airline Respirator	( ) Full face APR ( ) ½ face APR	( ) Cartridge Type _____ ( ) No respirator needed
Protective Clothing	( ) Fully encapsulated ( ) Tyvek F, with hood	( ) Saranex ( ) Coveralls, Cotton	( ) Work Clothes ( ) Other:
Gloves (specify inner/outer)	( ) Nitrile ( ) Butyl	( ) Neopene ( ) Latex	( ) Leather ( ) Cotton
Head/Face/Eye/Ear Protection	( ) Safety Glasses–ANSIZ87.1 ( ) Ear plugs or muffs	( ) Safety goggles ( ) Wire or Nylon Face Shield	( ) Hard Hat ( ) Other:
Foot/Leg Protection	( ) Work Boots ( ) Steel-toed boots	( ) Steel Toe covers ( ) Snake Leggings	( ) Chemical over boots ( ) Kevlar Leg Chaps
Other Protection	( ) Motor Cycle Helmet w/full face shield or goggles	( ) Hi-Visibility Vests	

5.1 PPE Modifications Required: Elevated PPE posture when dealing with suspected "Hanta Virus" locations.

6.0 Training Requirements

6.1-UXO personnel are EOD trained and approved by CEHNC-Huntsville
6.2-All Site personnel are OSHA qualified, both 40-hr and current 8-hr Refresher, IAW 29 CFR 1910.120
6.3- All Site personnel operating a vehicle maintain a current state driver's license.
6.4- UXO identification and safety precautions training for all Site Personnel. (Performed by UXOSO)
6.5-ATV operators will provide a copy of their qualifications and competency to the UXOSO, prior to any equipment operation.
6.6-Daily Safety and Operations Briefing. (Performed by UXOSO)
6.7-All Site personnel will attend "Site Specific Training" for safe work practices and hazard protection, IAW SSHP. (Performed by UXOSO).
6.8-Site personnel will be briefed on Material Safety Data Sheets (MSDS) for fuels and oils. (Performed by UXOSO)
6.9-Knowledge of emergency response and notifications IAW SSHP.
6.10-Maintain equipment IAW manufacturer's specifications and operate IAW owner's manual.

7.0 Equipment to be used and Inspection Requirements

Type	**Inspection Frequency (Daily/Weekly/Monthly)**		
Heavy Equipment (checks will be done prior, during and after operation)	Daily by Operator	Weekly as needed	Monthly as needed
First Aid Kits	Daily by Team Leader	Weekly by UXOSO for missing items	Monthly by UXOSO for expired items
Communications Equipment	Daily by Team Leader	Weekly by Team Leader	Monthly, as needed
Communication Checks w/radios (Cellular phones as back-up)	Twice Daily with all site elements. All "operations" will cease until communications have been re-established with at least another site element to relay information		
Fire Extinguishers	Daily by Team	Weekly by UXOSO	Monthly by UXOSO

8.0 Certification: The control methods, PPE and other procedures used in the conduct of this task have been selected as a result of a hazard assessment conducted by the individual identified below:

Printed Name: **Edward Grunwald, C.I.H., Project Safety and Health Officer** **Date: 01/20/05**

Accident Exposure Data Report
Parsons
Contract DACA87-00-D0038
Enter Date Here

Task Order No.	Name	Location	Total Field Hours Expended*	Vehicle Miles	Lost Workdays for month**	Total Lost Workdays	Number of Vehicle Accidents

* Including Subcontractors
**Due to On-the-Job Accidents

Ed Grunwald, Corporate Health and Safety Officer

Subject: Safety Of Use Message (SOUM), TACOM Control No. SOUM 03-xxx “Operational” Safety Of Use Message for ALL M-GATOR Vehicles.

D XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX D
A X "WARNING" X A
N X DEATH OR SERIOUS INJURY TO SOLDIERS, OR DAMAGE X N
G X TO ARMY EQUIPMENT WILL OCCUR IF THE INSTRUCTIONS X G
E X IN THIS MESSAGE ARE NOT FOLLOWED. X E
R XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX R

1. Distribution:

A. This Is An "Operational" Safety Of Use Message. MACOM Commanders Will Retransmit This Message to all subordinate Commands/Activities within 24 hours of receipt of this message and acknowledge receipt of this message within five working days to: CDRTACOM, Warren MI,AMSTA-LC-CIPWM, DSN 786-6096, Commercial (586) 574-6096 or DDN address: Safetyofuse@Tacom.Army.Mil.

B. MACOM Commanders will also track and report compliance of This message for all subordinate Commands/Activities to: the appropriate PEO/PM/WSM NLT (Approximately 30 Days).

2. Problem: John Deere M-Gator vehicles have been purchased through General Services Administration (GSA) catalog. The M-Gator is based upon a commercially available design. The M-Gator is a two-passenger, six-wheeled, all-terrain vehicle powered by a three-cylinder diesel engine. The M-Gator has a payload capacity of 1000 pounds, with a maximum ground speed of 17 miles per hour.

A. There has been no M-Gator vehicle use guidance published to document usage restrictions regarding occupants, speed, load, and towing limits. There exists the possibility for serious injury or severe vehicle damage if the M-Gator is operated without regard to the many warnings in the Commercial Off The Shelf (COTS) John Deere technical manual(s).

B. Unauthorized usage of the M-Gator can compromise the safety of Army personnel and equipment.

3. User Actions: Users are directed to limit usage of the M-Gator to these parameters:

A. The M-Gator cannot be used to evacuate litters or carry casualties.

B. Two occupants, front seats only. Load limits, 1000 lbs., must be followed. Helmet and eye protection are required for driver and passenger.

C. All loads over fifty pounds must be securely strapped to cargo tie-downs in the rear and to the cargo shelf in the front.

D. The M-Gator is not towable; damage to the Chain Drive, Transaxle and Tires will occur.

E. The M-Gator should NOT tow trailers, as it has not been evaluated for its ability to tow trailers.

F. The effects of airdrops have been minimally assessed. After Air Drop and prior to operation, the operator must visually inspect the M-Gator for damaged or loose components and for fluid leaks to ensure safe operation.

G. The M-Gator will not be driven on public roadways except to cross the roadway, and it will only be driven on a public roadway at designated crossing points or with a road guard.

H. Ammunition must be on a pallet and securely strapped down in the rear cargo area.

Unit Commanders, Contact your local TACOM Logistics Assistance Representative (LAR) or your State Surface Maintenance Manager upon receipt of this message for assistance. For assistance in Locating your TACOM LAR, See Paragraph 6C.

4. TACOM/PM actions: POCs below will be available to provide technical assistance concerning the M-Gator.

5. Supply Status: N/A

6. POC:

A. Darrel DeLamielleure, AMSTA-LC-CHLC, DSN 786-2721, delamied@tacom.army.mil

B. Vincent Kowalski, AMSTA-LC-CHLA, DSN 786-8037, Kowalskv@tacom.army.mil

C. To find your TACOM LAR, you must be a registered user in the Army Electronic Product Support (AEPS) database; if you are not a registered user, request access to AEPS at the public page https://aeps.ria.army.mil/aepspublic.cfm. Click on Enter AEPS, a security alert box will appear, click on "OK". Then a client authentication box pops up and you can click "OK" or "Cancel". That will bring up the enter-network password box where you will enter your user name and password and click "OK". Once logged into the AEPS site, click on Logistics Assistance Personnel Locator listed under popular applications. Then select the appropriate region, i.e.: CONUS, USAREUR, Far East, Kuwait. Select the location nearest you and click on a name. This will give you a LAR's name, DSN and commercial phone number, email address, and photo. If you don't have access to AEPS, you can also obtain this information by contacting the TACOM Senior Command Representative (SCR) for your area.

CONUS-East: includes all units east of the Mississippi, FORSCOM, SOUTHCOM, KUWAIT, and CONUS units deployed, (to include National Guard and Reserve units), DSN 236-6923, Commercial 910-396-6923.

CONUS-West: includes all units west of the Mississippi (to include all National Guard and Reserve units), DSN 737-0263,

Commercial 254-287-0263.

USAREUR: Great Britain, Germany, Belgium, Luxemburg, Italy, Bosnia, Kosovo, and Macedonia, DSN 314-375-3461, Commercial 01149 621-487-3461, in Germany, 0621-487-3461.

Far East: includes Alaska, Hawaii, Korea, Okinawa, Kwajlein, and Japan, DSN 315-722-3036/3579, commercial 011 82 32 520-6036/6579.

SBCT units can contact your SCR at DSN 357-2991, Commercial 253-967-2991.

Ground Safety Notification System
Risk Assessment

Subject: M-GATOR, JOHN DEERE ALL-TERRAIN VEHICLE

1. This risk assessment was prepared in accordance with the procedures and guidance outlined in AR 750-6, AR 385-16, and the TACOM Safety Office SOP "Assessing Risk for Ground Safety Notification System Message Classification."

2. System Identification: The M-Gator is a two-passenger, six-wheeled, all-terrain utility vehicle powered by a three-cylinder diesel engine. The cargo box behind the passenger seats measures 59.5" x 45.2" x 9.2", and has a payload capacity of 1250 pounds. The vehicle has a rated maximum ground speed of 17 miles per hour. This memorandum addresses assumed residual risks based upon available product information.

3. Problem Discussion:

a. Source of Problem: Tactical Vehicle CBU

b. Statistical data: There have been no failures documented to date of any mishaps occurring due to any of the following risks.

c. Background: Several CONUS and Deployed units purchased the John Deere M-Gator Utility Vehicle through GSA as an Administrative Use Vehicle. There are no stated tactical requirements for this system. John Deere has sold the M-Gator to Army divisions, Special Operations, and National Guard units. 101st Airborne recently was provided $4.1M for M-Gators.

The Defense Ammunition Center & School conducted a limited amount of testing and provided an interim test report dated 29 JUL 99, for ammunition transportability testing. No problems were noted – the vehicle tie-downs were deemed suitable for both tall and short loads, with a maximum capacity of 1000 lbs. However, no safety release for transporting ammunition was issued by Developmental Test Command. A Conditional Safety Release was issued by Developmental Test Command (DTC) dated 24 FEB 00, for 10th Mountain Division use during a Joint Contingency Force – Advanced Warfighting Experiment. This safety release was only valid for this particular exercise and no further DTC testing has been conducted. Currently, the M-Gator has not been evaluated for its ability to tow trailers, and the effects of airdrops have been assessed and documented in Test Report 2000-FD-ABN-1500F/CT-0501, *Low Velocity Airdrop of the M-Gator Military Utility Vehicle* of March 2001, conducted by US Army Operational Test Command, Airborne & Special Operations Test Directorate . If G-3 approves an Urgent Materiel Release, the package will contain a number of restrictions on its use, specifically to the

administrative environment it was designed to operate in. Its Gross Vehicle Weight stability and towing in rough terrain, noise, and vibration in uniquely military environments will be assessed by the DTC. Further testing will determine the extent of the residual hazards experienced in the uniquely military operational environment.

4. Hazard Classification

a. Severity: The M-Gator based upon is a commercially available vehicle design. It is considered safe as long as it is used for tasks it was designed for. However, it will be used at times outside of the commercial use envelope, i.e., air drop, transporting ammunition or casualties, operation in rough/unknown terrain, etc. This risk assessment is being prepared primarily with these non-commercial uses in mind. There exists the possibility for serious injury or severe vehicle damage if it is operated outside of the commercial use envelope, or without regard to the many warnings in the technical manual. There is no roll-over protection on this vehicle, therefore it is imperative that soldiers exercise caution and heed all warnings in the operators manual when operating the M-Gator. If a roll-over is experienced with one or more litters on board containing injured personnel, serious injury or death is likely to occur. From input provided by user activities, it has come to light that soldiers may be using the M-Gator as an ambulance to evacuate casualties off of the battlefield. Due to the above stated roll-over risks, the M-Gator may <u>not</u> be used to evacuate casualties or carry litters. Therefore, the severity category assessment is CATASTROPHIC (Category I). The definition of CATASTROPHIC is: death, system loss, or severe environmental damage.

b. Probability: The likelihood of severe injury or vehicle loss is assessed as REMOTE. Once again, if used for purposes that the commercially available Gator is used for, this vehicle may be considered safe for operation. However, use of this vehicle in a uniquely military environment places additional and sometimes unknown stresses upon the vehicle and occupants. These additional stresses have not yet been identified, and are in the process of being evaluated. The definition of REMOTE is: unlikely but possible to occur in the life of an item.

5. Risk Level: The above hazard classifications were determined from the Decision Authority Matrix for PEO GCSS managed systems. The U.S. Army Acquisition Executive (AAE) approved the matrix in November 1995. Since the risk to personnel safety in the event of a roll-over has been classified HIGH, I recommend that a Safety Of Use Message (SOUM) be sent to the field regarding this issue.

6. The following page shows the hazard severity categories, hazard probability categories, and PEO GCSS Managed Equipment Decision Authority Matrix.

//kbb// 31 MAR 03
KRISTIAN B. BARTON
Safety Engineer

Reviewed by:
//nls// 31 MAR 03
NICHOLAS L. STRAFFON
Safety Director

HAZARD SEVERITY CATEGORIES

Description	Category	Definition
Catastrophic	I	Death, system loss, or severe environmental damage
Critical	II	Severe injury or illness, major system or environmental damage
Marginal	III	Minor injury or illness, minor system or environmental damage
Negligible	IV	Less than minor injury or illness, or less than minor system or environmental damage

HAZARD PROBABILITY CATEGORIES

Description	Level	Specific Individual Item	Fleet or Inventory
Frequent	A	Likely to occur frequently	Continuously experienced
Probable	B	Will occur several times in the life of an item	Will occur frequently
Occasional	C	Likely to occur some time in the life of an item	Will occur several times
Remote	D	Unlikely but possible to occur in the life of an item	Unlikely but can reasonably be expected to occur
Improbable	E	So unlikely, it can be assumed occurrence may not be experienced	Unlikely to occur but possible

AMC Managed Equipment
Decision Authority Matrix

HAZARD SEVERITY		HAZARD PROBABILITY				
		A	B	C	D	E
		Frequent	Probable	Occasional	Remote	Improbable
I	Catastrophic	HIGH				
II	Critical					
III	Marginal		MEDIUM			
IV	Negligible					LOW

HIGH	-	Commanding General AMC
MEDIUM	-	Commanding General TACOM
LOW	-	Project Manager

Appendix I

Response to Comments

Army's Response to Comments from the US Environmental Protection Agency

Subject: Draft Generic Site-Wide
Sampling and Analysis Plan
Seneca Army Depot
Romulus, New York

Comments Dated: September 15, 2005

Date of Comment Response: October 10, 2005

Army's Response to Comments

GENERAL COMMENTS

Comment 1: DOD, USEPA, and DOE have adopted the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP), June 2005, as the standard format for preparing QAPPs for Federal Facilities. USEPA Region 2 has adopted this guidance for all Superfund, RCRA, and Brownfield projects within the Region. It should be noted that QAPPs previously prepared do not have to follow the UFP guidance, however, any site-specific QAPPs, a significantly revised generic QAPP, or any new QAPPs prepared for sites in Region 2 will need to follow this new format. It is recommended that a crosswalk between the generic SAP and the UFP-QAPP requirements be provided to ensure that all elements of the current guidance are incorporated. The reference pertaining to the UFP-QAPP is located at: http://www.epa.gov/swerffrr/documents/intergov_qual_task_force.htm.

Response 1: Acknowledged. It should be noted that a cross reference table was presented in Appendix A to provide a crosswalk between the contents of the generic SAP and the requirements of the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP). The UFP-QAPP examined while preparing the draft SAP was the July 2004 version. The March 2005 version has been examined and the crosswalk provided in Appendix A of the Draft Seneca Generic SAP is considered appropriate. The table has been revised to reference the May 2005 version UFP-QAPP.

Comment 2: **Revised Section 16.3.3 (Geophysical Surveys), page 85.** Unexploded ordnance (UXO) are not mentioned in this revised Sampling and Analysis Plan (SAP). However, UXO detection is an integral part of the sampling and investigations that will be conducted at this site. This deficiency should be addressed.

Response 2: Acknowledged. It should be noted that SOPs for surveys that are applicable for investigations at potential UXO sites (e.g., EM-31 survey and EM-61 survey) were presented in Section 16.3.3. Section 16.3.14 has been added to the SAP to present general procedures when sampling and investigating potential UXO sites.

Comment 3: **Revised Section 16.4.1 (Groundwater Sampling – Low Flow Purging and Sampling from Monitoring Well, Page 122 and by Appendix F that includes the EPA Region II Ground Water Sampling Procedures – Low Stress (Low Flow) Purging and Sampling, page 122.** Detailed standard operating procedures (SOPs) for field activities (e.g. low flow groundwater sampling, monitoring well installation, etc.) were not provided in the SAP. While the activities were discussed in general terms, the text should be revised to indicate that detailed SOPs must be submitted with each site-specific work plan.

Response 3: Disagree. Detailed standard operating procedures for low flow groundwater sampling were presented in Section 16.4.1. This section (page 122 through page 127 in the draft SAP) covers equipment to be used and detailed field procedures (Step 1 through Step 20 in the draft) for low flow groundwater sampling. In addition, Appendix F provides a 10-page low flow sampling SOPs developed by EPA Region 2. Information provided in Section 16.4.1, combined with the SOPs that were contained in Appendix F, provides the required detailed SOP for low flow groundwater sampling. The described sampling techniques will be followed, as appropriate, for groundwater sampling efforts anticipated in future work at the SEDA. Therefore, the Army does not plan to unnecessarily include the detailed SOP for each site-specific work plan (SS-WP). Rather, each site-specific work plan will discuss any variance to the base SOP for low flow sampling that is anticipated, if any, for all future groundwater sampling efforts.

Detailed SOPs for monitoring well installation, development, and abandonment were presented in Sections 16.3.5, 16.3.6, and 16.3.7, respectively.

Comment 4: **Section 16** was explained to include standard operating procedures for field investigation activities for indoor air/ambient air sampling (16.4.9) and for radiological surveys (16.4.11). Both these SOP sections are deficient and should be revised as noted below.

Response 4: Acknowledged. The radiological surveys section (Section 16.4.11) has been revised per the above comment and in response to the specific comments (i.e., Specific Comments 7, 8, and 9 for FSP) provided below. Section 16.4.9 was intended to provide general guidance to air sampling. SOPs for indoor air/ambient air sampling, if warranted, will be included in the site-specific work plan. Section 16.4.9 has been revised to reflect that detailed SOPs for indoor air/ambient air sampling will be included in the SS-WP.

SPECIFIC COMMENTS

Comment 1: **Section 3.1 Project Organization, page 6.** It is stated that a chart showing the project organization is presented in Figure 3. It should be noted, however, that the chart does not indicate a Quality Assurance Officer position, and subsequently, whether this position is independent of project information and data generation. This should be clarified.

Response 1: Agreed. Figure 3 has been revised to include a Quality Assurance Officer (QAO). Section 3.2.5.2 has been revised to clarify that the QAO will not be involved in the project data generation process but is responsible for reviewing project information and data to make sure the project work is conducted in accordance with the SAP.

Comment 2: **Section 3.2.5.2, page 9. (Formerly Section 3.2.4.2, page 8).** This section provides the duties of the Quality Assurance Manager (QAM). The QAM should be independent of the unit that is generating data. Such independence is not evident in Table 2 or Figure 3. Text should be revised accordingly.

Response 2: Agreed. It should be noted that it was the Quality Assurance Officer that was referenced in the SAP. Table 2 and Figure 3 have been revised to reflect the above comments. Section 3.2.5.2 has been revised to clarify that the QAO will not be involved in the project data generation process but is responsible for reviewing project information and data to make sure the project work is conducted in accordance with the SAP.

Comment 3: **Section 3.2.6 Subcontractor, page 11.** UPEPA Region 2 requires that the *Analytical Services Tracking System* (ANSETS) Data Requirement form to be submitted on a monthly basis to the USEPA Regional Sample Control Coordinator (RSCC) for all Non-CLP analytical data. The Region 2 RSCC is Jennifer Feranda at (732)321-6687, feranda.jennifer@epa.gov or Adly Michael at (732)906-6161, michael.adly@epa.gov.

Response 3: Acknowledged. The Army contacts all of its contractors quarterly (end of March, June, September and December) and requests that all data be reported to them in electronic format. The data from all contractors are then combined and sent in an electronic format to USEPA Region 2 and the NYSDEC. According to Adly Michael, an USEPA Region 2 Sample Control Coordinator, the Army does not need to submit the Analytical Services Tracking System Data Requirement form under this circumstance. A laboratory data submittal section (Section 8.11.4) has been added to the SAP to reflect that analytical data are submitted to USEPA Region 2 on a quarterly basis.

Comment 4: **Section 4.3.4, page 17. (Formerly Section 4.3.4, page 14).** This section discusses data completeness, and indicates that data with minor exceedances in accuracy and precision may be considered usable. The text should be revised to indicate that the acceptance of exceedances in accuracy and precision must be based on a data usability assessment, which is described in Section 8.7.

Response 4: Agreed. Section 4.3.4 has been revised to reflect the above comment.

Comment 5: **Section 5.3.2 Sample Handling, page 35.** It is stated in the last sentence of this section that Table 13 identifies personnel primarily responsible for ensuring proper handling, custody, and storage of field samples during the different stages of sample flow. It should be noted that Table 13 is the Inspection/Acceptance Testing Requirements for Consumables and Supplies. It is stated in **Section 5.3 Sample Handling and Custody** that Table 15 illustrates the sample handling system, which is the proper table number. This inconsistency should be corrected.

Response 5: Agreed. The last sentence of Section 5.3.2 has been revised to reference Table 15, which illustrates the sample handling system.

Comment 6: **Section 8.1 Data Review Requirements for Screening Data, page 43.** It is stated that the screening data methods are identified in Table 3 and the calibration and QC requirements are presented in Table 16. Subsequently, it is stated that the calibration, QC requirements, and corrective action requirements (required) are shown in Table 3. This should be corrected to read Table 16, or the sentence could be combined with the preceding sentence since it is redundant.

Response 6: Agreed. The last sentence of the first paragraph under Section 8.1 has been deleted therefore Table 3 is no longer referenced in this section.

Comment 7: **Section 8.6 Analytical Data Validation, page 54.** It is strongly recommended that 100% data validation will be performed.

Response 7: Acknowledged. The Army will require that 100% data validation be performed on analytical data developed under site investigations and remedial actions. The statement in the original document indicated that at least 20% of the validated data would be reviewed by the project chemist. The statement that 100% data validation will be performed has been added to Section 8.6.

FIELD SAMPLING PLAN (FSP)

Comment 1: **Section 16.3.6, page 102. (Formerly Section 16.3.7, page 71).** This section provides details on monitoring well development. A time interval between development and sampling was not provided. It is recommended that wells not be purged and sampled within 48 hours of development. Preferably, allow 1 week to pass between development and sampling. Additional information should be included in the text.

Response 1: Acknowledged. It should be noted that a time interval between development and sampling was provided in Section 16.3.5 (Groundwater Monitoring Well Installation). Nonetheless, Section 16.3.6 has been revised to restate the time interval of seven days between development and sampling.

Comment 2: **Section 16.3.11, page 114. (Formerly Section 16.3.12, page 75).** This section provides the decontamination procedure for sampling equipment (e.g. trowels and augers for soil sampling). No solvent rinse is specified. For analysis of metals, a diluted nitric acid rinse is recommended followed by a deionized water rinse. For analysis of organics, a reagent-grade isopropanol rinse is recommended followed by an analyte-free water rinse. Distilled water is not recommended for rinsing sampling equipment. The text should be revised. This information should also be added to Section 16.5.3.

Response 2: Agreed. Section 16.3.11.1 has been revised to incorporate the above comments.

Comment 3: **Section 16.4.1.2, page 123. (Formerly Section 16.4.1.2, page 77).** This section discusses groundwater sampling. Low flow sampling is the only method specified. Low flow sampling is not applicable in all situations, such as bedrock wells with long open boreholes in which the water bearing zones have not been characterized. As low flow sampling is not always applicable, an alternative method of purging and sampling should be added to the text.

In addition, the text should be revised to include key points of the sampling protocol:

- A specific method for submersible pump decontamination;
- Order of sampling wells from least to most contaminated;
- The stabilization parameter for ORP should be ± 10 millivolts;
- Stabilization parameter checks are in 5 minute intervals instead of 3;
- During sample collection for all parameters, the pump discharge should be low enough to prevent drawdown in the well, ideally between 100 and 250 milliliters per minute; and
- Provisions for wells that do not stabilize after 4 hours of purging.

For sampling dissolved metals, filtering procedures and specifications should be provided.

Response 3: Acknowledged. Only low flow sampling is discussed in this section as the Army anticipates that the majority of groundwater sampling at Seneca will be conducted using this method. Alternative sampling methods required for specific investigations or remedial actions will be addressed in the SS-WP. A statement has been added to Section 16.4.1 to state that alternative groundwater sampling methods (i.e., not low flow procedures) will be specified in the SS-WP.

For the key points of the sampling protocol indicated in the comments:

- Submersible pump decontamination was presented in Section 16.3.11 of the draft SAP. A sample equipment decontamination step has been added to the sampling procedures and a reference to the sample tubing and submersible pump decontamination processes has been added to the decontamination step.
- A statement has been added to Section 16.4.1 to reflect that order of sampling wells from least to most contaminated will be used when feasible. The stabilization parameter check was listed as ±10 millivolts, as recommended in the comment. No revision was made to the text.
- The interval between stabilization parameter checks was stated as 5 minutes in the draft SAP, which was consistent with the comment. No revision was made to the text.
- As stated in steps 13 and 14 of the field procedure, the pump discharge rate should be below 100 milliliters per minute for VOCs and below 250 milliliters per minute for all other analytes. The requirement was consistent with the comment and therefore no revision was made to the text.
- Provisions for wells that do not stabilize after five well volumes have been removed have been added to the field procedures. It is recommended that field personnel check instrument condition and calibration, purging flow rate and all tubing connections before deciding whether or not to collect a sample or to continue purging.

Filtering procedures have been added under Section 16.4.12.

Comment 4: **Section 16.4.6, page 135. (Formerly Section 16.4.1.7, page 80).** This section describes active soil gas sampling. Steps to prevent or detect ambient air intrusion into the sample should be added to the text. These steps may not be required for all sampling situations (e.g., high concentrations or methane sampling in the vicinity of a landfill), but all samples for inclusion in a risk assessment should include the following steps to prevent ambient air intrusion:

- Packing a hydrated bentonite seal around the probe at the ground surface;

- Conducting a leak test to make sure there are no leaks in the sampling train. Use a syringe to pull a vacuum prior to pulling up on the drive rod. If the vacuum is present, there are no leaks;

- Limiting the purge volume to the sum of the volumes of the tubing and the space below the drive rod when the rod is pulled up. The two liters specified in the text is too much for the shallow samples expected. With 10 feet of 1/8-inch tubing and a 1-inch space below the drive rod, approximately 42 milliliters (mL) would need to be purged. This can easily be done with a 60 mL syringe and a stainless steel three-way valve;

- Limiting the purge and sampling rate to no more than 200 mL per minute. In addition to increasing the chance for ambient air infiltration, higher rates can cause biased high concentrations by "stripping" contaminants adsorbed to soil particles. It is recommended that all purging (and sampling for Tedlar Bags) be done with a syringe to minimize the purge rate. The sampling rate should be similar to the purge rate. Flow regulators may be required to limit the sampling rate of summa canisters;

- It is recommended that a tracer compound be used to test for ambient air intrusion. The draft New York State Department of Health guidance (Guidance for Evaluating Soil Vapor Intrusion in the State of New York, Public Comment Draft, February 2005), recommends using a gas, such as helium or butane as a tracer. Another easier method is to use rubbing alcohol (2-propanol). Paper towels can be soaked with 2-propanol and place around the base of the drive rod, around the tubing where it exits the drive rod, and at any other connections or fittings. The 2-propanol will volatilize and will be detected in the sample at a high concentration if ambient air infiltration is significant.

Tygon tubing is specified. If the analytical data collected are for use in a risk assessment, Teflon® tubing must be used. Stainless steel ferrules and compression fittings may be used to connect the tubing to the sampling device.

The text specifies the use of an ambient air blank when using Tedlar® bags. If the blank is to be used to check the integrity of the lot of bags used for sampling, the blank should be filled with ultra-high purity nitrogen instead of ambient air. Ambient air contains many chemicals at trace amounts that may be detectable. It should be noted that Tedlar® bags can contain trace amounts of compounds, particularly petroleum hydrocarbons, and caution should be exercised in their use.

Response 4: Agreed. Section 16.4.6 has been revised to add the above specified steps for ambient air intrusion prevention. Whether the Tygon® or Teflon® tubing will be used will be specified in the SS-WP. The text has been revised to read "Tygon® or Teflon® tubing (as specified in the SS-WP)" instead of the original "Tygon® tubing". The section regarding Tedlar® bags has been revised to reflect potential trace contamination with the bags. The statement of the use of ambient air for the blank has been replaced by the specification of the use of pure nitrogen. In addition, a statement has been added to Section 16.4.6 that detailed design of soil gas sampling will be included in the SS-WP if needed.

Comment 5: **Section 16.4.9, page 141.** The section is entitled "Indoor Air/Ambient Air Sampling," but it is by no means clear which sampling discussion pertains to indoor air sampling and which pertains to ambient air sampling, nor for that matter, the reasons for presenting sampling methods only for metals and SVOCs. The first paragraph indicates that the section presents methods for collecting indoor air samples for metals and SVOCs, but the fifth and sixth paragraphs refer to ambient air sampling methods. The Tisch Environmental sampler cited in the fifth paragraph is a PM-10 sampler, not a total suspended particulate matter (TSP) sampler, as indicated (TSP is no longer a primary pollutant). The second paragraph, which reads, "three different methods were employed to collect air samples for metals," suggests that the text may have been borrowed from a report, rather than developed for use as an SOP.

In view of the previously cited NYSDOH draft guidance for soil vapor intrusion, an indoor air and outdoor air sampling procedure for volatile organic compounds should be added. Text should be revised.

Response 5: Acknowledged. It should be noted that this section was to provide general guidance on air sampling. SOPs for air sampling programs not covered in this section, if warranted, will be included in the SS-WP. The above statement has been added to Section 16.4.9. The title of Section 16.4.9 has been changed to "Air Sampling" to remove distinction

between indoor air and ambient air sampling. The reference to TSP has been replaced by PM_{10} and the future tenses have been used throughout the section.

Comment 6: **Section 16.4.10.3 Quality Assurance and Quality Control Samples, page 146.** For Trip Blanks it is stated that they are to be collected for all media. This is further clarified in **Section 16.7.3 Trip Blanks**, page 156, where it is stated that trip blanks are prepared only when VOC samples are taken and are analyzed only for VOCs. It should also be noted that it is not necessary to take an aqueous trip blank when a non-aqueous medium is being sampled.

Response 6: Acknowledged. It should be noted that the QA/QC samples discussed in Section 16.4.10.3 was only for wipe sampling (Section 16.4.10) only. Section 16.7.3 presents general trip blank requirements for all sampling efforts. A statement has been added to Section 16.7.3 indicating aqueous trip blank is not necessary for non-aqueous medium samples.

Comment 7: **Section 16.4.11.1, page 149.** The referenced Ludlum 43-68 is a gas proportional detector, not a phoswich. A count rate meter should be specified with this detector.

Many of the numbered steps in the procedure should be revised:

- Step 2. What check source?
- Step 3. How long is the calibration current?
- Step 6. Toggle switch is set to alpha + beta, but which meter?
- Step 11. Include copy of referenced survey form.
- Step 12. Parenthetic refers to beta counts only, but alpha should be indicated considering Step 6 directs setting the detector to alpha + beta.
- Step 13. Include connector cable as serviceable part.
- Step 15. Turn rate meter off, not "phoswich."

Include instrument manuals in Appendix G.

Response 7: Acknowledged. The procedures in the SAP have been modified to list general types of radiation detectors and instruments rather than specific instruments. Specific makes and models of the appropriate instruments will be determined by a health physicist based on availability and applicability if and/or when specific radioactive constituents are identified at areas of concern at SEDA. Instrument manuals and survey-specific procedures will be included in the SS-WP as necessary. The above statement has been added to Section 16.4.11. In addition, the requirement of specification of instrument makes and models, instrument manuals, and survey-specific procedures has been added to Section 17 (Requirements for SS-WP).

Comment 8: **Section 16.4.11.2, page 151.** The FIDLER is a detector, but the referenced Ludlum 2220 is a scaler/ratemeter. Moreover, the Ludlum 2220 is an outdated model that has been replaced with the model 2221. Provide the referenced survey forms.

Include instrument manuals in Appendix G.

Response 8: Acknowledged. As stated in the previous Response 7, the procedures in the SAP have been modified to list general types of radiation detectors and instruments rather than specific instruments. Specific makes and models of the appropriate instruments, instrument manuals, and survey-specific procedures will be included in the SS-WP as necessary. The above statement has been added to Section 16.4.11. In addition, the requirement of specification of instrument makes and models, instrument manuals, and survey-specific procedures has been added to Section 17 (Requirements for SS-WP).

Comment 9: **Section 16.4.11.3, page 152.** The Ludlum Model 19 is a microR meter, meaning micro Roentgen exposure rate meter, not a "micro rem dose rate instrument" as titled. Moreover, the meter measures exposure rate is µR/hr, not dose in rad/hr as indicated.

Many of the numbered steps in the procedure should be revised:

- Step 2. What check source?
- Step 3. How long is the calibration current?
- Steps 2 and 4 are the same, and Steps 3 and 5 are the same.
- Step 6. What action is associated with "be aware"?
- Step 10. What window? The NaI detector is mounted internally.
- Step 13. Micro-R meter, not Micro-Rem meter.

Include instrument manuals in Appendix G.

Response 9: Acknowledged. As stated in the previous Responses 7 and 8, the procedures in the SAP have been modified to list general types of radiation detectors and instruments rather than specific instruments. Specific makes and models of the appropriate instruments, instrument manuals, and survey-specific procedures will be included in the SS-WP as necessary. The above statement has been added to Section 16.4.11. In addition, the requirement of specification of instrument makes and models, instrument manuals, and survey-specific procedures has been added to Section 17 (Requirements for SS-WP).

Comment 10: **Section 16.7.1, page 156. (Formerly Section 16.4.4.1, page 84).** Ambient blanks are specified in this section. The text indicates that the sampling procedure for an ambient blank is the same as a conventional field blank. The definition indicates that ambient blanks will be used to assess the potential introduction of contaminants from ambient sources surrounding the sampling location. However, the text indicates that ambient blanks are collected only when VOC samples are collected and analyzed only for VOCs. Inorganics and other contaminants, however, can be introduced to samples, for example, during a confirmatory sampling effort at an active excavation site. Justification should be provided for analyzing only for VOCs.

Response 10: Acknowledged. The section of Ambient Blank has been removed from the report as this is not a requirement by the CLP program according to the Contract Laboratory Program Guidance for Field Samplers (USEPA, 2004) or the CLP Statement of Work for various analytical methods.

Comment 11: **Section 16.6, page 155. (Formerly Section 16.4.3, page 83).** This section provides sample custody information. Laboratory chain of custody documentation was not provided. The forms should be added to the SAP.

Response 11: Acknowledged. Specific requirements for laboratory chain of custody documentation were presented in bullet format under Section 16.6 in the draft SAP. Different laboratories can use different forms to document chain of custody as long as the requirements in the SAP are met. Therefore, a uniform laboratory chain of custody document is not provided in the SAP.

Comment 12: **Section 17.0 Requirements for Site-Specific Work Plan (SS-WP), pages 165-167.** It is stated that this section summarizes the key elements of the SAP that should be covered in the SS-WP. It should be noted that the following items, located within the QAPP and FSP, reference the SS-WP and should also be included in this listing:

a. It is stated in **Section 5.3.3 Sample Delivery, page 35** of the QAPP that "unless specified in the SS-WP, samples will be delivered directly to the lab." Sample delivery should be included in No. 14 of Section 17.0.

b. It is stated in **Section 9.2.2 Field System Audit Procedures, page 63** of the QAPP, that field audits, if warranted, should be specified in the SS-WP.

c. It is stated in **Section 16.3.2 Site Recon, Preparation, and Restoration Procedures, page 85** of the FSP, that the designated areas of decontamination shall be specified in the SS-WP.

d. It is stated in **Section 16.3.11 Equipment Decontamination, page 114** of the FSP, that decontamination methods will be modified, if necessary, based on the SS-WP.

e. It is stated in **Section 16.3.12.3 Disposal, page 121** of the FSP, that waste disposal companies and disposal facilities will be identified in the SS-WP.

f. It is stated in **Section 16.4.5 Wet Sediment Sampling, page 134** of the FSP, that unless specified in the SS-WP, sediment sample shall be collected with 6 inches into the sediments.

g. It is stated in **Section 16.8.1 Parameters, page 159** of the FSP, that any additional equipment needed for a specific project task shall be identified in the SS-WP.

Response 12: Agreed. The items listed in the above comments have been included in Section 17.0.

Comment 13: **Tables Section. Table 1-A. (Formerly Appendix E, Table 1-A, page E-4).** This table presents screening values and the preferred maximum method quantitation limits for soil/sediment. For 2,4,6-trinitrotoluene, the lowest human health screening value is 3.9 mg/kg (Region 3 RBC for an HQ=0.1), however the column entitled Most Stringent Human Health Criteria: Soil – Direct Contact is listed as 16 mg/kg, and the preferred maximum method quantitation limit is listed as 8 mg/kg. Review these values and resolve the apparent discrepancies.

Response 13: Agreed. Table 1-A has been checked with the various referenced sources (e.g., Region 3 RBC table) and revised to be consistent with these references. The column entitled Most Stringent Human Health Criteria: Soil – Direct Contact has been checked for consistency. The column entitled Preferred Maximum Method Quantitation Limit has been removed and the method quantitation limit requirement will be presented in the SS-WP based on site-specific information.

Army's Response to Comments from the New York State Department of Environmental Conservation

Subject: Draft Generic Site-Wide Sampling and Analysis Plan
Seneca Army Depot
Romulus, New York

Comments Dated: November 23, 2005

Date of Comment Response: December 8, 2005

Army's Response to Comments

Comment 1: Section 4.4.2 Method Detection Limit Verification – This section appears to allow MDL verification by analyzing one sample. However MDL must be established annually based on seven spiked samples. This should be clarified.

Response 1: Acknowledged. It should be noted that this section (Section 4.4.2) presents method detection limit verification, which can be performed by analyzing one sample. Method detection limit establishment, which should be conducted annually based on seven samples, is discussed in the preceding section (Section 4.4.1).

Comment 2: Section 4.5.4 Surrogates – This section cited a limit of 10% surrogate recovery. The usual methods use either in-house derived upper and lower limits or method advisory limits.

Response 2: Agreed. The section has been revised to cite Table 8 for surrogate recovery limits. Table 8 assembles surrogate recovery limits for various analysis methods. It should be noted that Section 4.5.4 has been renumbered to Section 4.5.5.

Comment 3: The section on the EM61-MK-2 Metal Detector, near the back of the book, has some figures missing and some blank pages. The section is to that extent incomplete.

Response 3: Agreed. The missing figures and blank pages in the EM61-MK-2 Metal Detector manual (Appendix G) have been updated.

Comment 4: In multiple places in the document, references to the Air Force are made when submitting records, data, log books, etc. What does the Air Force have to do with the Seneca Army Depot Activity? Clarification is requested.

Response 4: Acknowledged. Several Seneca projects now use an Air Force contract vehicle so the Air Force is referenced in the Sampling and Analysis Plan which was submitted under an Air Force contract.This Draft Final Generic Site-Wide Sampling and Analysis Plan is submitted under the Huntsville contract and there is no reference to Air Force in this report.

Comment 5: I understand that this document is an umbrella document under which project-specific tasks are conducted and that specific site-related analytical issues may be incorporated into the specific site work plan document. However, a statement regarding deviations, such as modified or updated analytical methods, from the generic SAP must be incorporated into the site-specific workplan and approved by the regulatory agencies prior to the start of field work. Revisions to the generic SAP may be necessary in the future based on new regulatory analytical criteria mandated by the legislature or the Agencies.

Response 5: Acknowledged. Any QA/QC and field sampling protocols that are different from or not covered in the generic SAP will be presented in the SS-WP. This is stated in Section 17 (Requirements for Site-Specific Workplan) of the generic SAP. Detail of SAP revision is covered under Section 13 (SAP Revisions and Distribution) of the report.

Army's Response to Comments from the New York State Department of Environmental Conservation

Subject: Final Generic Site-Wide Sampling and Analysis Plan
Seneca Army Depot
Romulus, New York

Comments Dated: February 21, 2006

Date of Comment Response: March 31, 2006

Army's Response to Comments

SPECIFIC COMMENTS

Comment: It is noted that the section 4.4.2 Method Detection Limit Verification remains problematic. The Army state "An MDL verification check…can be performed quarterly in place of the annual MDL study" and the next sentence "However this may not substitute for the initial MDL determination." While these sentences may be open to differing interpretations, it seems to me that Army are stating that the one sample study may or may not substitute for the MDL study. It is my understanding that it may NOT take the place of the MDL study. Perhaps my understanding of the requirements is wrong but this still needs to be clarified.

Now it is a good idea to run these MDL checks and when they fail to pass, they propose to change the MDL to a higher value. This would change other limits as well such as Quantitation limits and the question arises whether the limits required by the contract remain intact. Another proposal would be to consider a verification failure to be a problem and the cause(s) determined and corrected so that the MDL value as determined by the seven sample study be maintained. For example if the cause is loss in instrument sensitivity, then that should be addressed by suitable instrument maintenance (new inlet liner, column trim etc.). Now if that is the case then other criteria would probably be out of control also. On the other hand perhaps the problem is a spiking error and then only a new spiking standards need be made up and the MDL is maintained.

Response: Acknowledged. The Army proposes to run an MDL study using procedures that are consistent with those described in 40 CFR, Part 136, Appendix B. Once the initial MDL study is performed and documented, the laboratory has the option of either repeating the MDL study once per year or running quarterly MDL verification checks to verify the continuing validity of the initial MDL study.

The Army's proposal regarding MDL study and MDL verification in the Final SAP is consistent with the federal regulation (40 CFR, Part 136, Appendix B), the USACE requirements presented in the Engineering and Design - Requirements for the Preparation of Sampling and Analysis Plans (USACE EM200-1-3, 2001), the AFCEE specifications presented in the Guidance for Contract Deliverables (AFCEE, 2005), and common laboratory practices performed by various NY CLP and NELAC certified laboratories such as STL Buffalo.

Sections 4.4.1 and 4.4.2 have been revised to restate and clarify the Army's MDL study and verification proposal. In addition, the above proposals presented in the comment on MDL check result handling have been incorporated in Section 4.4.2. The Army's revised text for these two sections is provided below for review.

4.4.1 Method Detection Limit Study

The MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence when the analyte concentration is greater than zero. The MDL is lower than the concentration at which the laboratory can quantitatively report. Laboratories determine their "best case" sensitivity for analytical methods by performing MDL studies. The MDL determinations are required at initial analytical method set-up. After the initial study, the MDL determinations shall be performed once per 12 month period, or otherwise be replaced by quarterly MDL verification, as discussed in the following section. In addition, the MDL studies shall be conducted when a major change to the analytical method, instrumentation, or preparation (e.g., extraction) procedure occurs. The MDL study shall be conducted by following the procedure as described in 40 CFR 136 Appendix B. The MDLs achieved by the chosen laboratory within one year prior to the analysis of project samples should be less than or equal to one-half the sample reporting limits.

4.4.2 Method Detection Limit Verification

An MDL verification is performed on an MDL check sample spiked at approximately 2 times the reported MDL to confirm the MDL or to extend the use period of the MDL. The MDL verification can be performed on each instrument immediately following an MDL study to validate the MDL. In addition, after the initial MDL study, the MDL verification can be performed quarterly in lieu of the annual MDL study. The MDL verification sample shall be taken through all the preparatory and determinative steps used to establish the MDL values. The MDL is verified if the laboratory can reliably detect and identify all analytes in the check sample by the method-specified criteria. If the method has no confirmation criteria, the check sample must produce a signal that is at least 3 times the instrument's noise level. If the MDL is not verified, one of the following three measures should be implemented by the laboratory:

- determine the cause(s) of the verification failure, correct the problem, and repeat the MDL verification.
- spike the MDL check sample at successively higher concentrations until the verification criteria are met, and use the first successful concentration as the reported MDL. The laboratory and project chemist shall ensure the newly established MDL still meets the PQOs.
- reconduct the MDL study.